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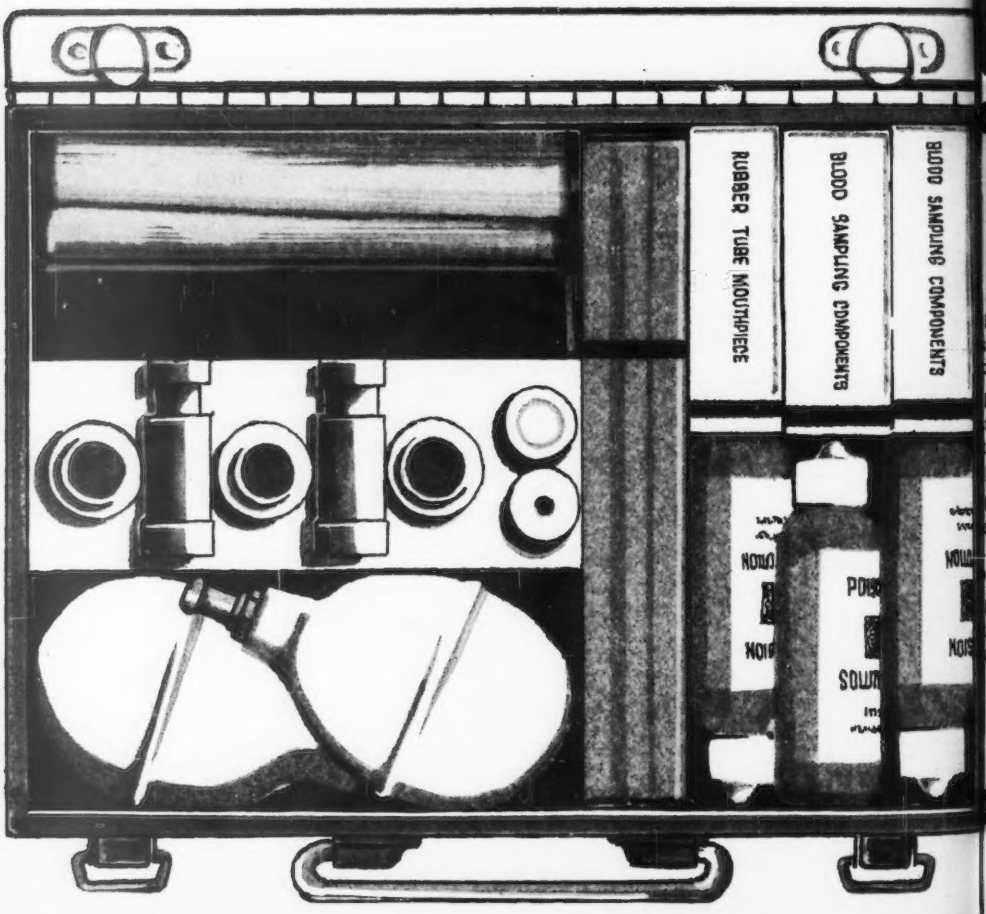

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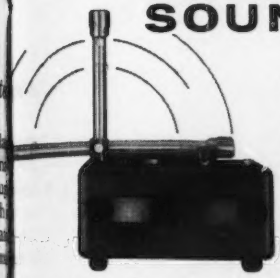

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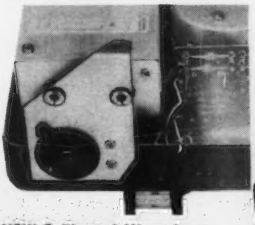

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President's Page

Comparison of the scientific achievements of the United States with those of Russia is the order of the day. Apart from spatial hardware, intercontinental ballistics missiles and nuclear weapons there are the less spectacular matters of industrial hygiene and its practice in the two countries.

We do not have enough information comprehensively to evaluate Russian industrial hygiene theory and practice but several differences between U.S.S.R. and U.S.A. views are at once apparent in a paper by S. B. Smeljansky which was presented at the Twelfth International Congress on Occupational Health held in Helsinki in July, 1957. For example, standard orders pertaining to maximum allowable concentrations of toxic substances in the air of workrooms are "legal regulations and are obligatory for all plants of the Soviet Union." Russian MAC's are derived for the most part from studies of the effects of toxic substances on conditioned reflexes—a method of testing claimed to have greatly superior sensitivity. The MAC's are but a fraction of those generally accepted in the United States—one-twentieth in the case of lead, one-tenth for mercury, one-fourth for carbon monoxide and so on.

A difference in the regulatory aspect of MAC's in the two nations is to be expected, our government philosophies being what they are, but such great variances in the MAC's themselves can hardly be justified. At first glance it appears that some of the Soviet values may be based on pharmacological effects so minor as to outlaw the coffee break if this pleasant custom were classed as an industrial exposure. Other standards appear to be highly impracticable or even impossible for industry to meet. But final judgment must be reserved because of our scanty knowledge of Russian science and industry.

Better communication would be helpful. Recently the National Science Foundation published a list of Russian scientific journals available in English, the majority of the translations being sponsored by NSF or by the National Institutes of Health. Absent are journals specifically concerned with industrial hygiene. Since such esoteric publications as *Teoriya Veroyatnostei i Primenenie* (Theory of Probability and its Applications) and *Voprosy Onkologii* (Problems of Oncology) are among those listed, it may not be too much to ask that translations into English of one of the principal Russian journals of industrial hygiene—*Gigiena i Sanitariya* perhaps—be made available.

Kenneth W. Nelson

AMERICAN

Industrial Hygiene ASSOCIATION Journal

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American Industrial Hygiene Association Journal, published bi-monthly for the American Industrial Hygiene Association. Dohrman H. Byers, *Editor;* Jack C. Radcliffe, *Associate Editor;* Lloyd E. Gordon, *News Editor.* Editorial Offices, 1014 Broadway, Cincinnati 2, Ohio. Subscription $7.50 per year in the United States; $7.75 per year in Canada; $8.25 per year in all other foreign countries. Single copies $1.50. © Copyright, 1959, by The Williams & Wilkins Co. Entered as second class matter at the post office at Baltimore, Md. The American Industrial Hygiene Association Journal reserves the right to edit all advertisements and to refuse advertising copy when it does not meet the high standards adopted by the Association.

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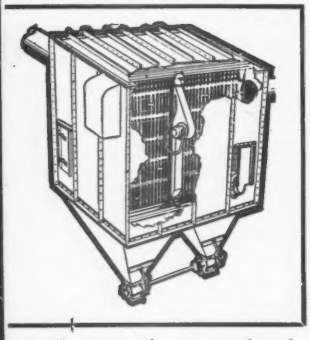

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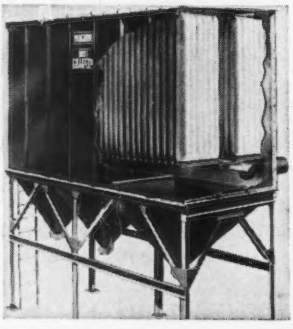

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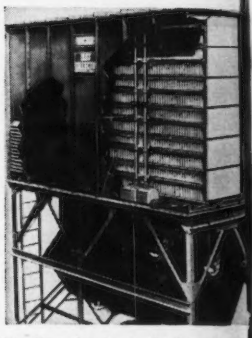

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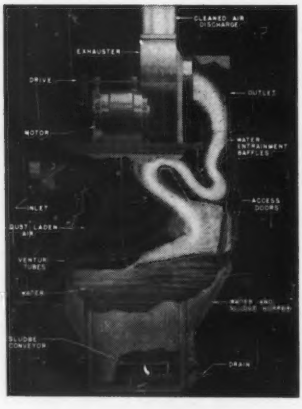

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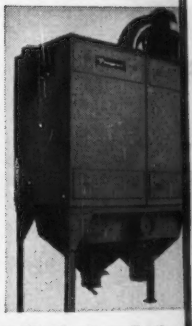

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A Recording Thermistor Globe Thermometer

ANDREW D. HOSEY

U. S. Department of Health, Education, and Welfare, Public Health Service, Occupational Health Program, 1014 Broadway, Cincinnati, Ohio

IN THE spring of 1956, this laboratory was requested to assist in an environmental heat study involving about 1700 employees in an 18-acre, hanger-type building, located in a midwestern State. Following the usual preliminary survey, it was agreed that data should be collected to estimate effective temperatures and the heat stress index proposed by Belding and Hatch.[1] Since the study was to extend over a period of at least two months, it was desirable to utilize recording instruments insofar as possible. Environmental factors needed to estimate effective temperatures and heat stress indices were: (1) ambient air temperature, (2) wet bulb temperature (or relative humidity), (3) air velocity, and (4) globe (black ball) temperature.

Continuous recording instruments were available at that time for air temperature and relative humidity but were not available for globe temperatures or low velocity air flows usually encountered in industrial plants (0 to 200 linear feet per minute). In view of this and the knowledge that several investigators were studying the effects of the heat exposure to military personnel (recently reported in the literature by Stallones et al.[2] and Yaglou and Minard[3]), there was a definite need for developing a new instrument; one which would be compact, portable and record not only the ambient air temperature and relative humidity but also the globe temperature and air velocity.

Thermocouples have been used for many years by several investigators[4, 5] to provide continuous recordings for integrating effective radiations from all sources. However, this usually involves the use of bulky and expensive equipment. It was decided, therefore, to investigate the use of thermistors for this purpose.

Thermistors, a contraction of the words thermally sensitive resistors, consist of complex metallic-oxide mixtures usually made from oxides of manganese, nickel, copper, cobalt, and sometimes from mixed crystals such as $ZnTiO_4$. Thermistors, while known to scientists for more than 100 years, were not generally available until the middle nineteen thirties. They can now be purchased in a variety of types for many uses.

Several reports on the use of thermistors for measuring the temperature of air, skin and liquids appeared in the technical literature during the past few years. In 1949, Pennman and Long[6] described a portable bridge for micrometeorology among growing crops. A modification of Pennman and Long's apparatus was made by Smith,[7] who claimed that the thermistor hygrometer agrees with the Assman psychrometer under most conditions. Stoll[8] and McLean[9] described instruments employing thermistors for measuring skin temperatures, and Howes[10] discussed the characteristics and applications of thermally sensitive resistors or thermistors in *Electrical Communication* in 1955.

Recording Globe Thermometer

As so often happens when a study is to be done, time is the limiting factor. It was decided, therefore, to concentrate our efforts on the construction of a recording globe thermometer to be used with available recording hygrothermographs and a heated thermoanemometer to collect data for this particular heat study. After several weeks of planning and "bread board" experimental setups, the apparatus shown in Figure 1 was evolved to record globe temperatures only. Two of these instruments were constructed by a local electronics engineer for $125 each (excluding recorders). They were operated continuously during the study for nearly 2½ months with no difficulty in the electronic circuitry of the detector or sensing unit. Figure 2 is a schematic wiring diagram of the unit including a list of the components.

The thermistor sensing element was calibrated first by immersing it in a constant temperature water bath, gradually raising the temperature of the water and comparing the output from the bridge circuit with readings of a standard thermometer. Using the components shown in Figure 2, the 5K ohm potentiometer attached to the bridge circuit was adjusted so that 100°F gave a 0.5 milliamp (ma) output on the Esterline-Angus recorder. Since the midpoint on the recorder scale (0.5 ma) was arbitrarily chosen to represent 100°F, it was necessary to set the recorder

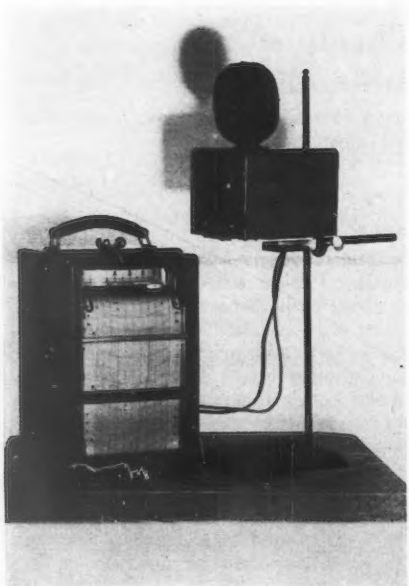

FIG. 1. Thermistor globe thermometer and power supply connected to recorder.

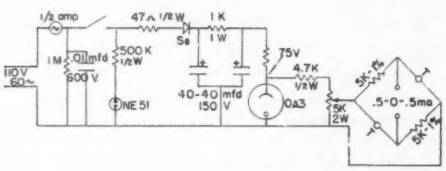

FIG. 2. Thermistor thermometer.

zero adjustment to 0.44 ma with the leads from the sensing unit attached but with no power on. In this manner, 0 to 1.0 ma represents a temperature range of from 75°F to 125°F estimated in ½-degree increments (½ scale division). For example, 0.4 ma = 95°F and 0.6 ma = 105°F.

This range could be altered within certain limits by heating the thermistor bead to 115°F, for example, and adjusting the 5K ohm potentiometer so that the bridge output was 0.5 ma. If this were done, the temperature range could be extended from 90 to 140°F. For this particular study such a high range was not considered necessary.

After the sensing element was calibrated in the above manner, it was sealed into the center of a 4-inch diameter toilet float previously painted inside and out with a dull black finish and mounted on top of the chassis as shown in Figure 1. Further calibration of the apparatus was accomplished by comparing its readings with a conventional globe thermometer; both instruments being placed at varying distances from a source of radiant heat. The thermistor responded much faster to temperature changes than the ordinary globe thermometer, thereby necessitating a longer waiting period for the two to reach equilibrium. Agreement between the two instruments was well within ±½° in the temperature range tested, 80 to 125°F.

A recorder chart speed of three inches per hour was used because of the pen lag. However, the recorders were overhauled during the study and their response to change was greatly improved so that slower speeds were satisfactory. Figure 3 is a section of one chart, selected at random, between the hours of noon and 3 p.m. on September 12, 1956, at one location in the plant. This is presented to show a typical response of the instrument. The power to the sensing unit was turned off about 1 p.m. to check the calibration and the recorder reached its calibration point (0.44 ma) at 1:20 p.m. but was allowed to operate until 1:40 p.m. when the power was again turned on. It will be noted that the globe temperature reading quickly returned to the position it was at 1 p.m., namely 0.4 ma or 95°F.

During the three-hour period represented by this section of the chart, the air temperature (recorded by a hygrothermograph located at the same height above the floor and adjacent to the globe sensing unit) at noon was 89°F, at 1 p.m. 90°F, at 2 p.m. 92°F, and at 3 p.m. 93°F. Corresponding globe temperatures were 93°F, 95°F, 96°F and 97°F. Thus at this particular time and in this location globe temperatures were 4° to 5° above the ambient air temperatures. The average difference between globe and air temperatures at all sampling stations for the 2½ month period was 3° or less. Since there were no sources of high radiant heat in this building, this factor was neglected in calculating effective temperatures. On the other hand, this study afforded an opportunity for a thorough test of the two instruments under actual plant conditions.

Figure 4 shows all of the instruments used in the aforementioned heat study. It is included here to point out some of the disadvantages with the then available equipment. These are: (1) No continuous record of air movement was available; instead plant personnel took periodic readings with the thermoanemometer and noted the results on a daily log sheet. (2) It was necessary to change charts on the hygrothermograph and globe temperature recorder weekly and to re-ink the three pens at that time. (3) In order to tabulate the data collected during the study it was

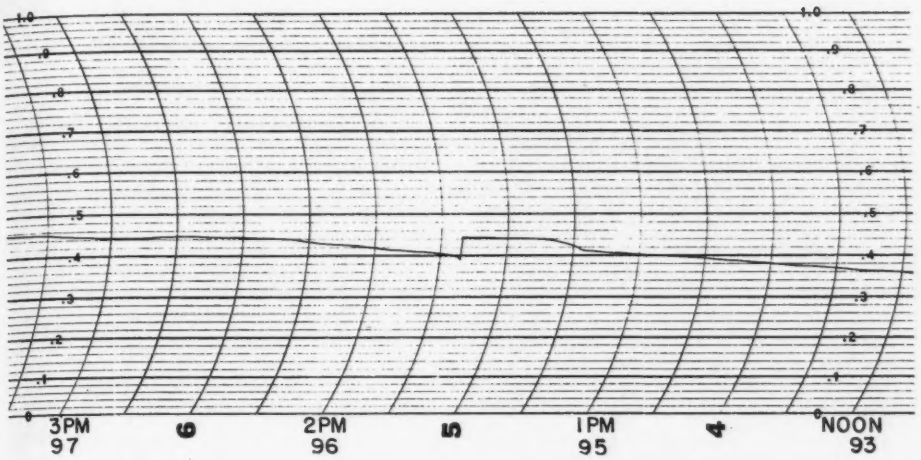

FIG. 3. Section of chart from noon to 3 p.m., September 12, 1956, showing typical response of instrument. Chart speed is 3 inches per hour, 1 division equals 15 minutes.

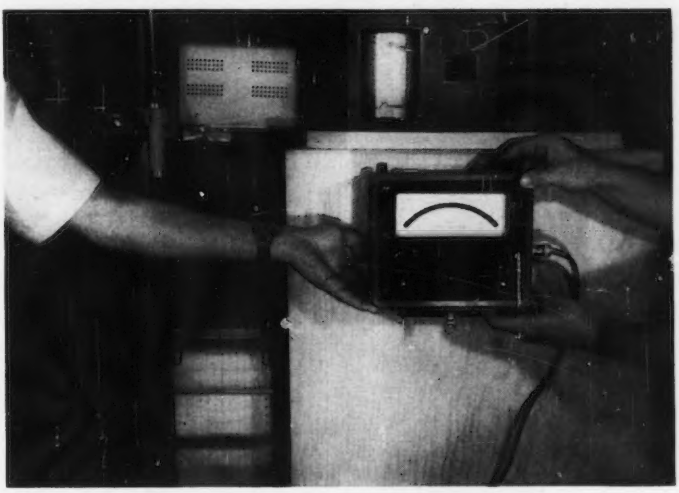

FIG. 4. Instruments used for collecting environmental heat stress data.

necessary to refer to two sets of charts and a daily log sheet.

Other disadvantages could be cited but these were enough to indicate the desirability for a single instrument capable of recording, on one chart, the four environmental factors necessary to evaluate heat stress.

Such an instrument, slightly larger than the recording globe thermometer shown at the left in Figure 4, was constructed and is being calibrated. A subsequent paper will describe its construction, calibration, and operating characteristics.

Summary

The need for a recording globe thermometer became apparent when this laboratory was requested to assist in a heat study at a large aircraft plant. An instrument, utilizing thermistors as the sensing unit, was developed for this purpose. It was used successfully during the

two and one-half month study to record continuously globe temperatures.

Acknowledgments

Assistance given by my colleagues in reviewing this paper and their constructive comments is gratefully acknowledged. Particular thanks are due to Mr. Howard L. Kusnetz for the drawings and Mr. David A. Fraser for the photograph of the globe temperature recorder.

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AIHA Annual Banquet

DR. KENNETH McFARLAND will be the speaker at the annual banquet meeting of the American Industrial Hygiene Association on Wednesday, April 29, 1959, in Chicago, Illinois. Dr. McFarland is educational consultant and guest lecturer for the General Motors Corporation, through whose courtesy he shall be our speaker. He has been a school executive for more than 24 years, is recognized as an authority in vocational education, and has a wealth of background and experience in a number of other fields. In a survey conducted by the U.S. Chamber of Commerce he was named "America's number one speaker". The AIHA banquet and Dr. McFarland's talk will be the highlights of the 1959 Industrial Health Conference.

Colorimetric Determination of Boron Hydrides by Means of Phosphomolybdic Acid*

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Department of Occupational Health, University of Pittsburgh, Pittsburgh, Pennsylvania, and Pharmacology Branch, Directorate of Medical Research, U. S. Army Chemical Warfare Laboratories, Army Chemical Center, Maryland

MICROANALYTICAL procedures for the determination of boron-hydrogen compounds have been very few and of late origin. Etherington and McCarty[1] described a semiquantitative method involving the use of a soluble silver-amine complex with which they were able to spot-test for diborane, pentaborane and decaborane. Hill and Johnston[6] developed a very specific procedure for the determination of decaborane by means of a quinoline reagent, which gives a red color with decaborane, or by means of ultraviolet (UV) spectroscopy of the solutions of decaborane in aqueous alkaline media. Feinsilver[2] discovered that diborane can be determined very conveniently by brominating it with a solution of bromine in glacial acetic acid and ultraviolet spectroscopy of residual bromine. Hill, Levinskas, and Novick[3] showed that an iodometric macrotitration is useful for the determination of microquantities of at least one of the amine-boranes, namely dimethylamine-borane. Hill, Gipson, and Heacock[4] found that N,N-diethylnicotinamide gives a red color with decaborane, but not with diborane and pentaborane, and that this color is produced even in aqueous solutions to which the quinoline method of Hill and Johnston[6] is not applicable.

It had been noted by Hill and Gipson[5] in some work on blood of animals treated with decaborane that a blue color was obtained in the performance of phosphorus analyses by the Fiske-Subbarow method at the point of adding ammonium molybdate to the acid solution and before the addition of aminonaphtholsulfonic acid. This clearly indicated the presence of reducing substances. Furthermore, it had been observed at an early date in the work with boranes in the two respective laboratories of the authors that during dynamic tests with decaborane a fleeting blue color was obtained if the air current containing the borane was passed through a phosphomolybdic acid solution. Theoretically this agent should lend itself to the determination of boranes on account of the great reducing power of the latter compounds and their derivatives. Dynamic testing was found to be applicable if the air current was passed through an alkaline medium, such as aqueous NaOH, in order to abstract the borane from the air, possibly in the form of a hypoborate, and if such solutions were then added to a large excess of phosphomolybdic acid solution (modified Folin and Wu reagent). Obviously an alkaline agent was necessary for abstraction of the decaborane from the air current, but an acid medium was needed to bring about the blue molybdate color. While a substantially straight line relationship was observable over a considerable part of the standardization curve, the method was not considered sufficiently promising in view of better methods then in the developmental stage[6], and work on the phosphomolybdate reaction was temporarily shelved.

When emphasis of the work shifted from simple boranes to their reaction products with various amines (i.e., the amine-boranes) it was discovered that the latter could not be determined by means of the quinoline reaction, so that a search for applicable methods became imperative. A return to the phosphomolybdic acid method brought immediate success. All of the nitrogen adducts of boranes with which we have come in contact yield the typical molybdate blue color when brought together with aqueous acid solu-

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tions of phosphomolybdic acid, though the speed of color development varies with the several compounds investigated.

The blue color is also produced by pentaborane and by sodium borohydride[10], under like conditions.

In the interest of conservation of journal space the authors decided to pool the experiences gained in their respective laboratories and to publish a more comprehensive paper than otherwise could have been done. This accounts for a certain heterogeneity in the design of the experiments, in the instruments used, and in the treatment of the experimental results.

Procedures

Procedure 1: A stock solution is prepared by dissolving 5 mg of decaborane in 5 ml concentrated aqueous ammonium hydroxide and making up to 100 ml with distilled water. Varying volumes of this solution, equivalent to 5 to 50 micrograms of decaborane, are diluted to 5 ml in Klett colorimeter tubes with a 2.5% aqueous solution of phosphomolybdic acid (Fisher Scientific Co. Cat. No. A-237), acetate buffered at pH 3.7. Then 5 ml of 1*N* HCl is added, and the color intensity of the solutions is determined in a Klett-Summerson colorimeter with a No. 66 filter. Constancy of color intensity is usually obtained after one hour, and linearity is observed at all intervals.

Procedure 2: A sample of 0.0565 gram of decaborane (0.0500 gram of boron) is dissolved in 25 ml of 0.6*N* NaOH; this may take about one half hour. The solution is diluted to 250 ml with distilled water to yield a stock solution containing 200 micrograms of boron per ml. Appropriate dilutions are then made to yield standards containing 2, 4, 6, 8, and 10 micrograms of boron per ml respectively. One ml of each of these standards is pipetted into Coleman cuvettes and 9 ml of phosphomolybdic acid solution (Folin and Wu as modified by Andes and Northup, Fisher Scientific Co. Catalog No. So-A-114) is added to each tube. The mixture is shaken and left standing for color development with the cuvettes closed by rubber stoppers. The intensity of the color thus produced is measured in a Coleman Junior Spectrophotometer at a wavelength of 670 millimicrons. About one hour

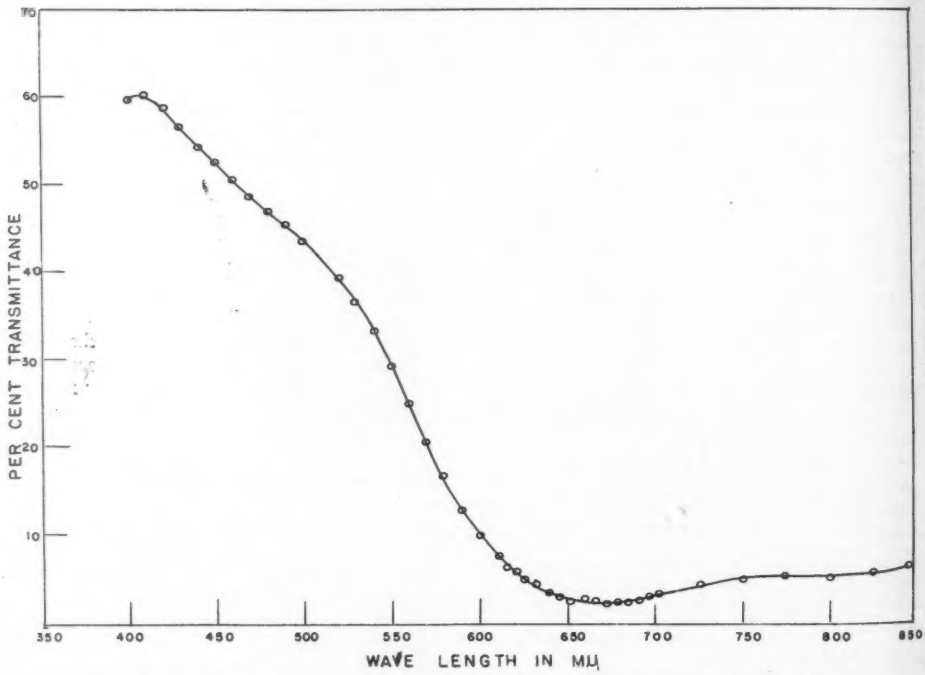

FIGURE 1. Spectral transmittance curve of blue color produced from a solution of decaborane in aqueous NaOH and phosphomolybdic acid solution (Folin and Wu as modified by Andes and Northup).

should be allowed for color development and operations must be timed carefully since the color increases in intensity for many hours and does not come to a steady state.

Procedure 3: A quantity of 0.2723 gram of dimethylamine-borane (0.0500 gram of boron) is dissolved in water and made up to 250 ml. This stock solution contains 200 micrograms of boron per ml. The rest of the procedure follows that of procedure 2.

Procedure 4: A stock solution of trimethylamine-decaborane is prepared by dissolving 5 mg of this compound in 100 ml of glacial acetic acid. Varying volumes of this solution, equivalent to about 50 to 300 micrograms of trimethylamine-decaborane, are diluted in Klett colorimeter tubes to a 10 ml volume with a 2.5% solution of phosphomolybdic acid (grade noted in procedure 1) in glacial acetic acid. The color intensities of the solutions are measured after three hours in a Klett-Summerson colorimeter using a No. 66 filter.

Procedure 5: Sufficient sodium borohydride is dissolved in 0.53*N* NaOH to furnish a solution containing 500 micrograms of boron per ml. This solution is diluted tenfold to yield a stock solution containing 50 micrograms of boron per ml. Appropriate dilutions of this stock solution are made to yield standards containing 2, 4, 6, 8, 10, 12, and 14 micrograms of boron per ml. All dilutions are made with 0.53*N* NaOH. One ml each of these standards is pipetted into Coleman cuvettes and 9 ml of phosphomolybdic acid (same preparation as used in procedure 2) is added to each tube. The cuvettes are closed with rubber stoppers, the mixtures are briefly shaken to mix, and set aside to permit the color to develop. Maximum intensity is reached after about one hour, and determinations are then made in a Coleman Junior Spectrophotometer at a wavelength of 665 millimicrons. Exact timing is necessary because the color fades gradually from the time of mixing but reaches a fairly steady state after the indicated time interval.

Discussion and Results

Light absorption of the blue phosphomolybdate solutions is strongest at a wavelength of about 660–670 millimicrons, as is seen from Figure 1. There may be slight variations for different boron-hydrogen compounds, but they cannot be significant.

Standardization curves for decaborane, dimethylamine-borane, trimethylaminedecaborane

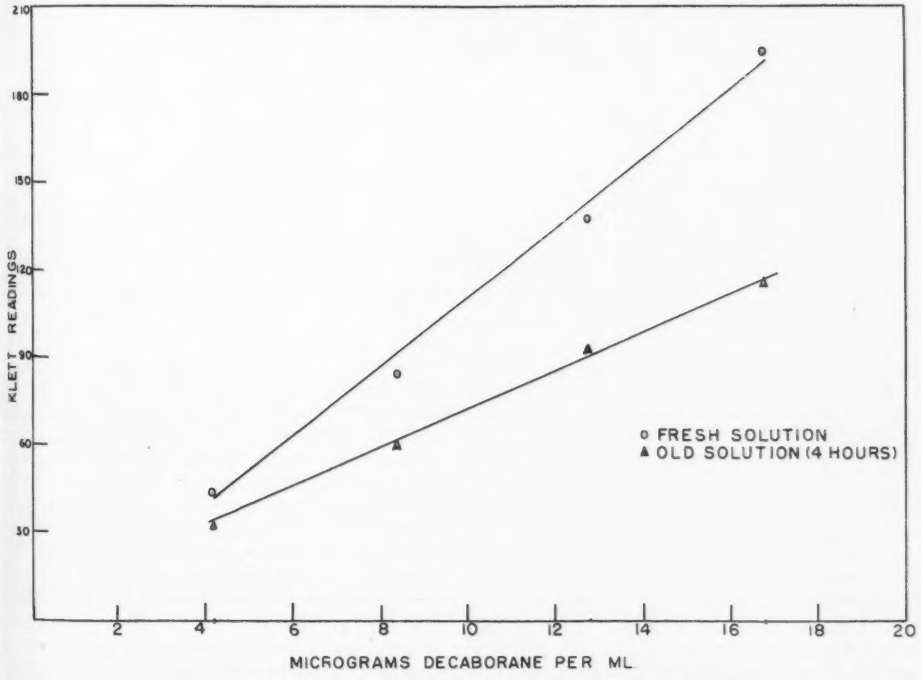

FIGURE 2. Standardization curve for decaborane by procedure 1.

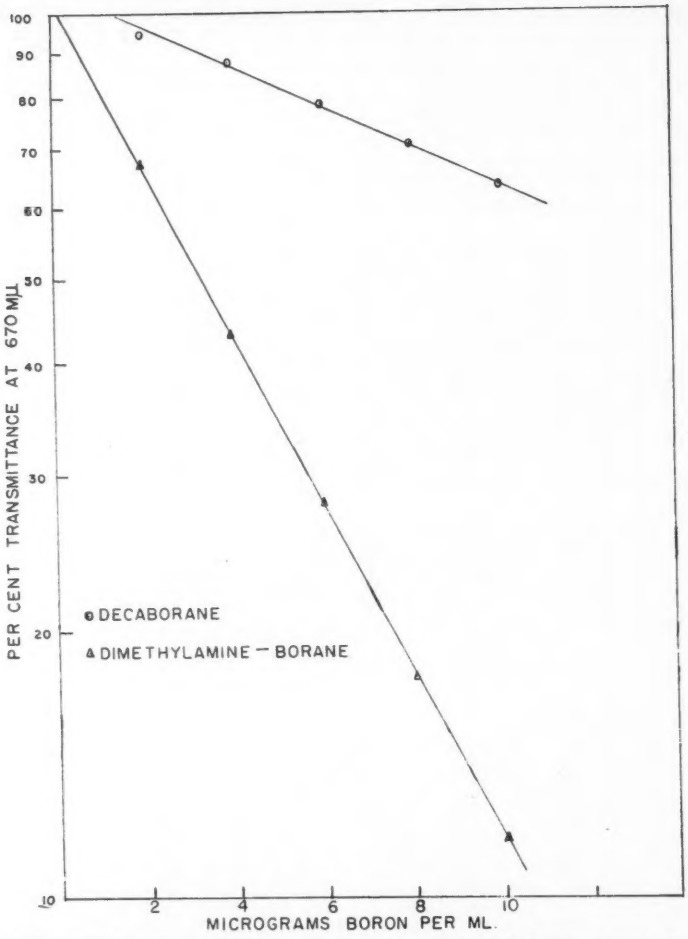

FIGURE 3. Standardization curves for decaborane and dimethylamine-borane by procedures 2 and 3 respectively.

and sodium borohydride are shown in Figures 2, 3, 4, and 5 respectively and the underlying data are given in Tables I through V. They represent substantially straight lines and it is evident, therefore, that the solutions follow Beer's Law in the range of concentrations investigated.

Solubilizers: Some of the boron hydrides are easily soluble in water while others are not. In the latter case auxiliary agents must be used to bring the materials into solution. Such agents may be solvents, such as ethanol, propylene glycol, or glacial acetic acid, or they may be alkaline compounds, such as aqueous NaOH, aqueous ammonia, pyridine, triethanolamine, trimethylamine, triethylamine, etc. Such alkaline materials probably react with some of the boranes with the formation of hypoborates, and their solutions in water show ultraviolet absorption as has been pointed out by Hill and Johnston[4] and has been found by Hill and Heacock.[5] On the other hand, adducts such as dimethylamine-borane seem to be constituted differently, for their aqueous solutions show no ultraviolet absorption. Even solvents such as ethanol may not really function as inert solvents but may react with the boranes to form derivatives more readily soluble in water. In any event, and whatever the constitution of such derivative compounds,

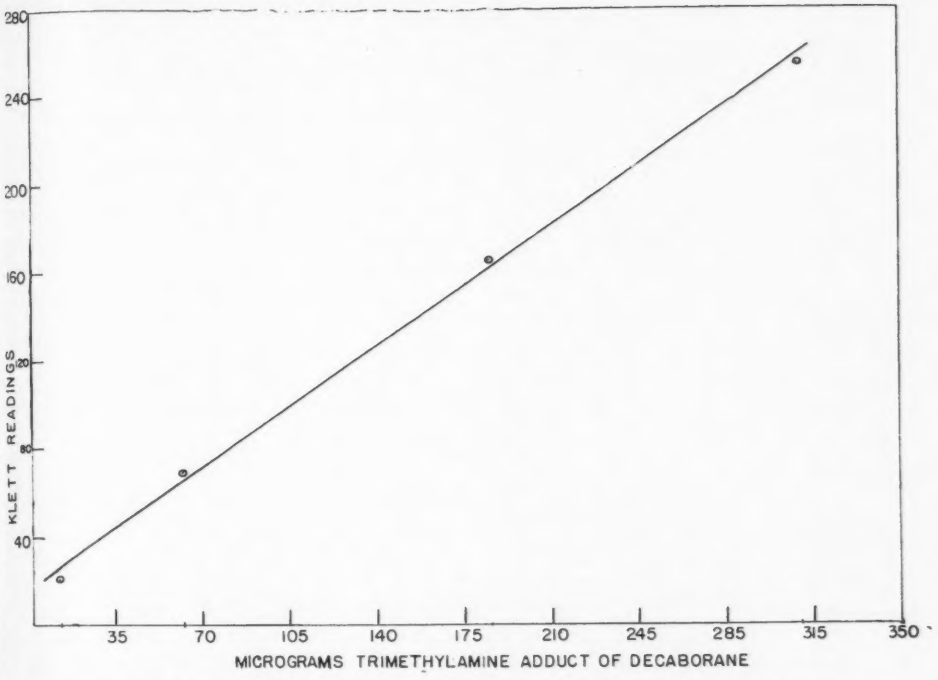

FIGURE 4. Standardization curve for trimethylamine-decaborane by procedure 4.

their aqueous solutions all react with phosphomolybdic acid to give a blue color. In order to avoid overlapping absorption patterns it is desirable to use one solubilizer only rather than a mixture, e.g. ethanol and NaOH.

Reaction Conditions: The phosphomolybdic acid reaction with boron hydrides does not occur with decaborane per se. If the latter is dissolved in glacial acetic acid it does not react therewith as is indicated by an unaltered infrared spectrum. If a 2.5% solution of phosphomolybdic acid (grade noted in procedure 1) in glacial acetic acid is added to such a solution, there is no production of blue molybdate color at any decaborane concentration tested and within the observed time interval of two hours. If, however, water or methyl alcohol is added to such a solution of decaborane in glacial acetic acid, either before or after addition of the phosphomolybdic acid solution, a blue color is developed. Thus it is appearent that decaborane per se does not react and that the formation of reducing intermediates is obligatory for producing the blue color with molybdate. Decaborane derivatives, on the other hand, give the reaction in glacial acetic acid without the intermediary of water or methyl alcohol. Derivatives tested in this manner were the ammonia, trimethylamine and pyridine adducts. They were prepared by passing ammonia, trimethylamine and pyridine respectively into 5% solutions of decaborane in carbon tetrachloride at room temperature, removing excess reagent by flushing with dry air, separating the solid adducts by filtration, and drying. Details of the preparations and the chemical and physical properties of the new compounds will be described in a separate publication.[5]

It was also observed that the reaction of boron hydrides with phosphomolybdic acid generally does not take place satisfactorily under alkaline conditions. For instance, if in procedure 1, the hydrochloric acid is left out, there is relatively little color development, and linearity is not obtained in three hours.

It is often advantageous to keep the mixture of boron hydride and reagent at an elevated temperature, e.g. at 50°C in a water bath, for the time of color development. More intense colors are obtained in this way, the waiting pe-

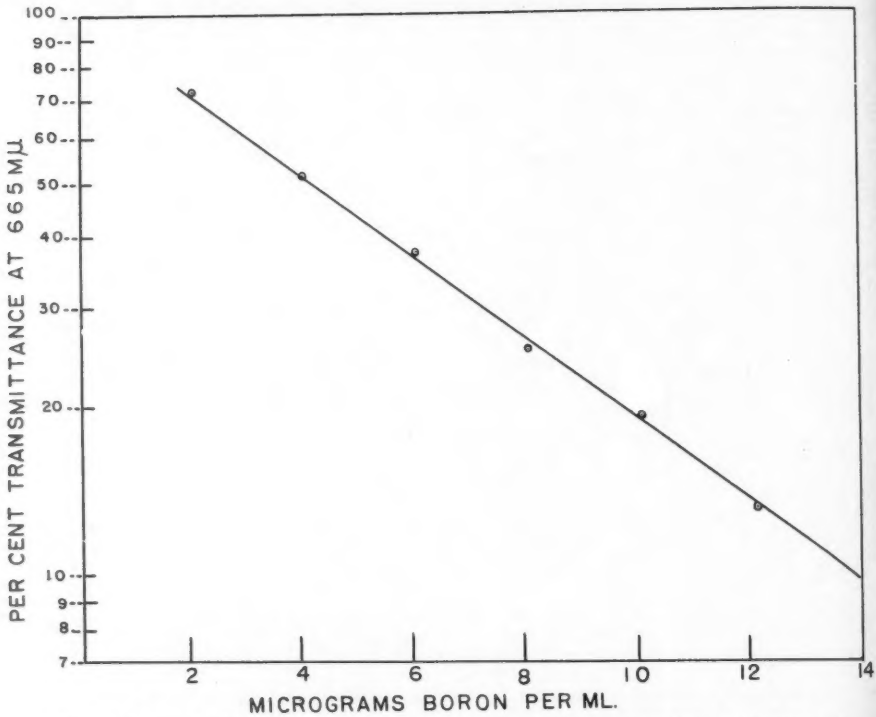

FIGURE 5. Standardization curve for sodium borohydride by procedure 5 (mean of 3 runs).

TABLE I

Reaction of Phosphomolybdic Acid with Solutions of Decaborane in Ammonium Hydroxide

Micrograms decaborane in solution	Klett readings of			
	Fresh decaborane solution		4-Hour old decaborane solution	
	1 hour after mixing	2 hours after mixing	1 hour after mixing	2 hours after mixing
4.2	44	44	32	33
8.4	85	87	58	59
12.6	139	140	92	92
16.8	194	194	115	115

TABLE II

Reaction of Phosphomolybdic Acid with Solutions of Decaborane in Aqueous NaOH

Minutes after mixing	% Transmittance of solutions containing				
	2 Micrograms boron	4 Micrograms boron	6 Micrograms boron	8 Micrograms boron	10 Micrograms boron
10	95.5	92.0	84.9	79.8	72.2
30	94.5	88.0	79.0	71.5	63.0
45	93.6	86.3	76.6	68.2	59.8
60	92.4	84.4	75.5	66.0	57.3
120	91.5	81.5	71.6	63.2	54.8
180	90.2	79.0	69.1	60.5	52.1
300	87.2	75.6	64.5	56.5	48.0

riod can often be shortened, and linearity is increased.

Hydrolysis: In analyzing compounds by this method, it is important to bear in mind that some of them are hydrolyzed quite readily in the presence of water, and this process may be speeded up considerably if alkalies and especially acids are present. However, the compounds do not all behave in like manner. Decaborane hydrolyzes much more slowly than either diborane or pentaborane (but the process is fast enough to be reckoned with, see Figure 2 and Table I). Sodium borohydride is stabilized to a

TABLE III

Reaction of Phosphomolybdic Acid with Solutions of Dimethylamine-Borane in Water

(Readings made 30 minutes after mixing)

% Transmittance of solutions containing				
2 Micrograms boron	4 Micrograms boron	6 Micrograms boron	8 Micrograms boron	10 Micrograms boron
67.7	43.3	28.0	17.6	11.7

TABLE IV

Reaction of Phosphomolybdic Acid with Solutions of Trimethylamine-Decaborane in Glacial Acetic Acid

Micrograms trimethylamine-decaborane in solution	Klett readings, hours after mixing					
	1	2	3	4	5	48
12.4	7	12	21	24	26	44
62.0	38	53	68	78	85	169
186	103	132	165	189	200	452
310	160	203	256	294	325	750

considerable degree in alkaline solution, as was pointed out by Lyttle et al.[11], and some of the amine-borane adducts, such as pyridine-borane, are quite resistant to hydrolysis. It is best, therefore, to prepare solutions fresh for analysis to avoid degradation of the boron hydride as much as possible. Careful timing as to all of the steps involved in the analysis is strongly recommended.

Applicability: The method is believed to be applicable to all boron hydrides, though some modification may be desirable for the one or the other compound, as is already indicated by the diversity of the procedures enumerated. It has been applied in our laboratories to the following compounds: decaborane, decaborane ammonia adduct ($B_{10}H_{14}\cdot NH_3$), decaborane trimethylamine adduct [$B_{10}H_{14}\cdot(CH_3)_3N$], decaborane pyridine adduct ($B_{10}H_{14}\cdot C_5H_5N$), decaborane triethylamine adduct [$B_{10}H_{14}\cdot(C_2H_5)_3N$], dimethylamine-borane [$(CH_3)_2NH\cdot BH_3$], trimethylamine-borane [$(CH_3)_3N\cdot BH_3$], pyridine-borane ($C_5H_5N\cdot BH_3$) and sodium borohydride ($NaBH_4$). Formation of the blue molybdate color has been observed with pentaborane dissolved in Cellosolve, but no quantitative work has been carried out. In view of these facts it may well be said that the method is not specific for any one boron hydride but is rather uni-

TABLE V

Reaction of Phosphomolybdic Acid with Solutions of Sodium Borohydride in 0.53*N* NaOH

(75 minutes after mixing)

	% Transmittance of solutions containing						
	2 Micrograms boron	4 Micrograms boron	6 Micrograms boron	8 Micrograms boron	10 Micrograms boron	12 Micrograms boron	14 Micrograms boron
Test 1	73.0	50.5	38.5	25.0	21.0		
2	74.0	52.5	37.5	27.5	17.5	13.0	10.0
3	72.0	51.0	36.0	22.5	18.5	13.0	9.5
Total	219.0	154.0	112.0	75.0	57.0	26.0	19.5
Mean	73.0	51.3	37.3	25.0	19.0	13.0	9.7

TABLE VI

Analysis by the Carmine Method of Dimethylamine-Borane Solutions Used in Establishing a Standard Curve

Micrograms boron, postulated per ml	% Transmittance at 625 millimicrons, against blank	Micrograms boron, found per ml	% of postulated value
2.0	74.5	2.1	105
4.0	57.7	4.0	100
6.0	44.0	6.0	100
8.0	34.2	7.9	99
10.0	27.0	9.6	96

TABLE VII

Analysis of Dimethylamine-Borane Samples by the Phosphomolybdic Acid Method

Sample (stock sol.)	Micrograms dimethylamine borane per ml, dilution theoretical	% Transmittance at 670 millimicrons, against water	Micrograms boron, from standard curve, per ml	Micrograms dimethylamine borane per ml, dilution found	% of theoretical value
1, (0.0051 gram)	5.1	83.6	0.9	4.9	96
	10.2	68.0	1.8	9.8	96
	20.4	43.2	4.0	21.8	107
	40.8	16.5	8.4	45.8	112
	51.0	11.5	10.1	55.0	108
2, (0.0134 gram)	2.68	93.2	0.4	2.2	83
	5.36	82.2	1.0	5.4	101
	8.04	74.9	1.4	7.6	95
	10.72	67.5	1.9	10.4	97
	13.4	58.1	2.6	14.2	106
3, (0.0114 gram)	4.59	86.5	0.7	3.8	83
	11.4	65.2	2.0	10.9	96
	22.8	40.2	4.3	23.4	103
	45.6	14.5	9.0	49.0	108

versally applicable to all of those that exhibit reducing power under the conditions of analysis.

The method has been used for the assay of boron hydrides and for the monitoring of air containing them. An example of the latter application is given in a paper by Hill, Levinskas, and Novick[8] on a method for monitoring boron hydrides by means of iodimetry. In that particular case both methods were compared with each other and the phosphomolybdic acid method was found to give results of sufficient accuracy to satisfy monitoring needs. The method has also been used in a study aimed at correlating the toxicity of the boranes with their chemical activity.[7]

Accuracy: In order to test the accuracy of the method, three different samples of dimethylamine-borane (0.0051; 0.0134; 0.0114 gram) were weighed out, made up to 100 ml volumes and diluted to "standards". The latter were analyzed by the above method using a standard curve obtained as outlined under procedure 3. Great care must be taken in weighing out dimethylamine-borane (especially when producing the standard curve) because this compound will absorb moisture readily if atmospheric humidity is high. To make sure that the solutions used for establishing the standard curve actually contained the amount of boron which they were supposed to contain, they were analyzed for boron by the Carmine method.[9] Table VI shows that they were within ±5% of the postulated values.

When the three sets of "unknown" solutions referred to above were subjected to the phosphomolybdic acid method of analysis and the transmittance values of the solutions thus obtained were evaluated by means of the standard curve, good checks were obtained except for boron levels which give transmittances in the less accurate ranges of the spectrophotometer used. The spread of values amounts to about ±10% and is generally closer to ±5%. Table VII gives the actual results obtained.

Conclusions

It is shown that phosphomolybdic acid reacts with various boron hydrides or derivatives thereof to form blue solutions. The intensity of the color thus produced is a linear function of the concentration of the boron hydride involved, and it can be used for the microanalysis of the compound. Depending on the procedure and the spectrophotometer used, linearity is obtained for concentrations of boron hydrides of from about 1 to 14 micrograms (as boron) per ml of standard or of solution tested by procedures 2, 3, and 5 and the Coleman Junior Spectrophotometer, and from about 1 to 300 micrograms of the chemicals (not as boron) for the other procedures and the Klett-Summerson colorimeter. Exact timing of the procedures is necessary because the colors increase or decrease with time depending on the boron hydride involved.

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Industrial Hygiene Foundation

THE INDUSTRIAL HYGIENE FOUNDATION announced at the twenty-third Annual Meeting in October, 1958, the election of Dr. William P. Yant as Chairman of the Board of Trustees, and the appointment of Dr. H. H. Schrenk as Managing Director. Dr. Yant is Director of Research and Development at Mine Safety Appliances Company. Dr. Schrenk was Research Director of the Foundation since 1949 and succeeds Dr. Richard Walmer as Managing Director. Both Dr. Yant and Dr. Schrenk have had long and outstanding careers in industrial hygiene, and are internationally known for their many contributions to the field.

A Multiple Chamber Exposure Unit Designed for Chronic Inhalation Studies*

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THE STUDY of chronic inhalation toxicity in animals over a period of years poses many problems in chamber design. For the best scientific and economic returns, the exposure chamber should have a capacity sufficient to hold a large number of long-lived species, such as, the dog and the monkey, it should be aerodynamically sound, and it should operate with few repairs during the entire period. In addition, the unit should fit within existing building space, be reasonable in cost, and if possible, be usable later for other or smaller scale studies.

An exposure unit currently used at Rochester in a five-year long study of uranium dioxide (UO_2) meets these requirements by incorporating a number of unique features. The new unit is a multiple chamber installation comprising four individual chambers, each having an internal volume of approximately two cubic meters. One aerosol generator supplies pre-ground UO_2 dust to the four chambers through a common inlet air system. Figure 1 is a photograph showing a rear view of the installation. The chambers are installed in a semi-circular arrangement in front of the master control panel, some of the instruments can be seen in the background through the chamber windows. Each chamber has its own exhaust air duct (below) which contains an airflow meter and a control valve. A scrubber for the effluent air stands at the left. An identical fifth chamber (not shown) is installed in the same general laboratory area and is used to house control animals.

Figure 2, a schematic top view, illustrates more clearly the arrangement of the chambers facing the control panel and the plan for introducing the UO_2 dust into the inlet air duct.

Briefly, the airflow pattern through the installation is this. Filtered and conditioned room air is supplied to the five-inch inlet air duct by a Clarage fan. The UO_2 dust is introduced, under slight positive air pressure, into the throat of a venturi mounted in this duct and the dust-laden air is transported through the duct and into a plenum chamber. The individual chambers, which operate at a slight negative pressure, draw aliquots of the dusty air from the plenum through their respective inlet air ducts. The dust and air mixture is admitted tangentially to the short cylindrical section at the top of each chamber. In this way, the air and the test material are mixed and distributed uniformly into each chamber as a result of a mild swirling motion.

The exhaust air is drawn axially from the bottom of each chamber through 2½-inch copper ducts, through a header and into a main 5-inch exhaust line which is connected to a Roto-clone exhaust fan. After several stages of filtration the exhaust air is discharged through an outside stack.

The individual exposure chambers are basically full-size replicas of the stainless steel chamber first described by Wilson and Laskin.[1] This type was selected because tests have shown that chambers of this design have two characteristics that are essential for accurate inhalation studies; namely, good airflow pattern and uniform contaminant distribution. Another advantage of this design is that it allows for maximum visibility of the animals. Because these chambers can be fabricated in any good sheet metal shop, their cost is not excessive (current price is about $2,000 per chamber). Stainless steel was chosen as the main construction material for two reasons; it is easy to clean and it is corrosion-resistant.

Each chamber has an animal capacity equivalent to eight beagle dogs, four monkeys and 40 rats. These animals are exposed at two elevations within the chamber. The top level which includes a rotating element supports monkey and rat cages. The purpose of this element is to facilitate loading of the caged animals. It does not rotate

* This work was performed for the Atomic Energy Project, Contract W-7401-eng-49.

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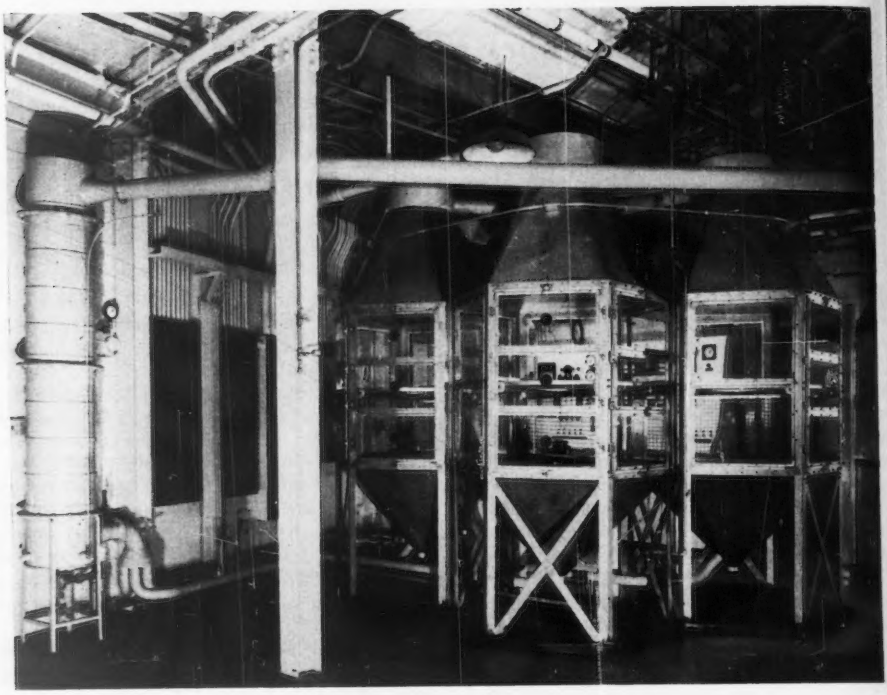


FIGURE 1.

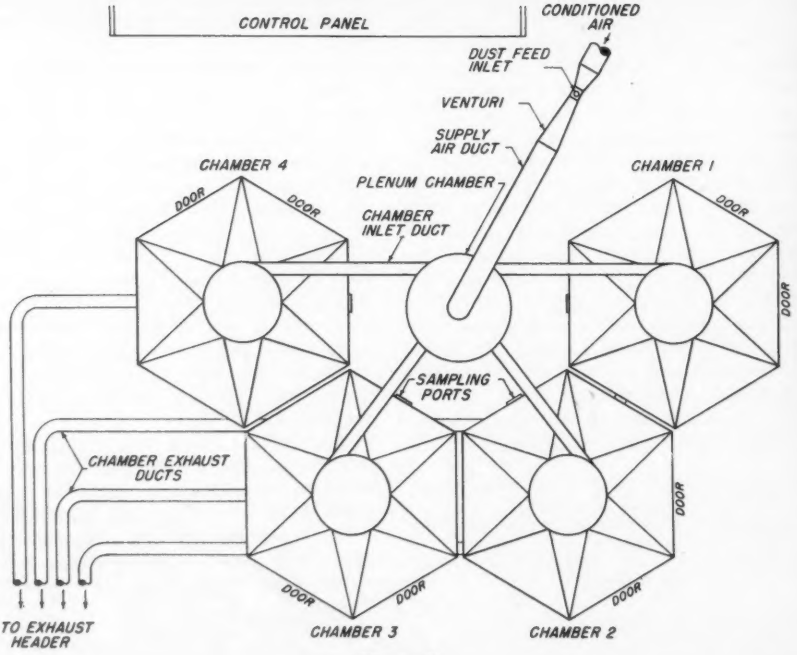
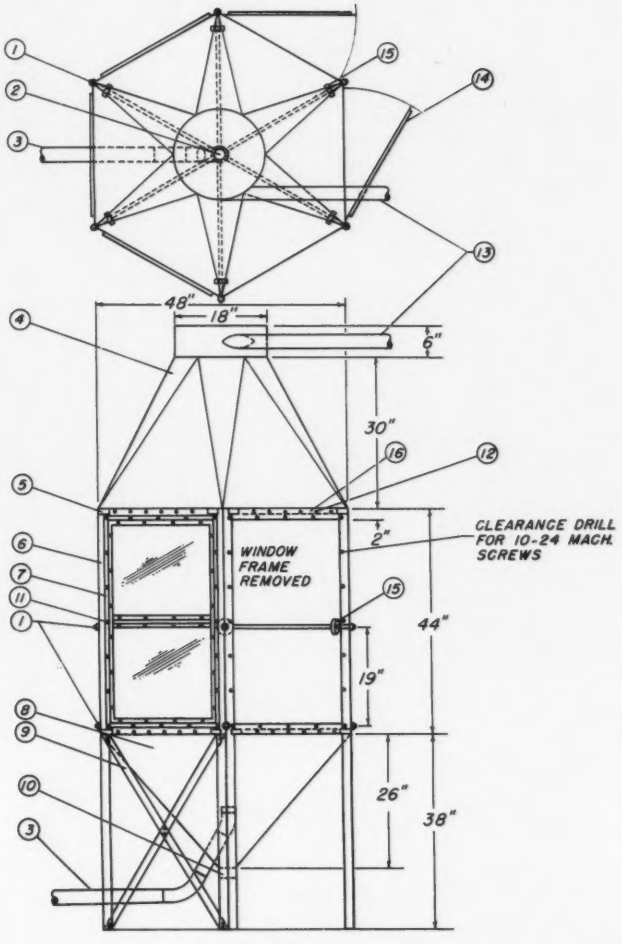


FIGURE 2.



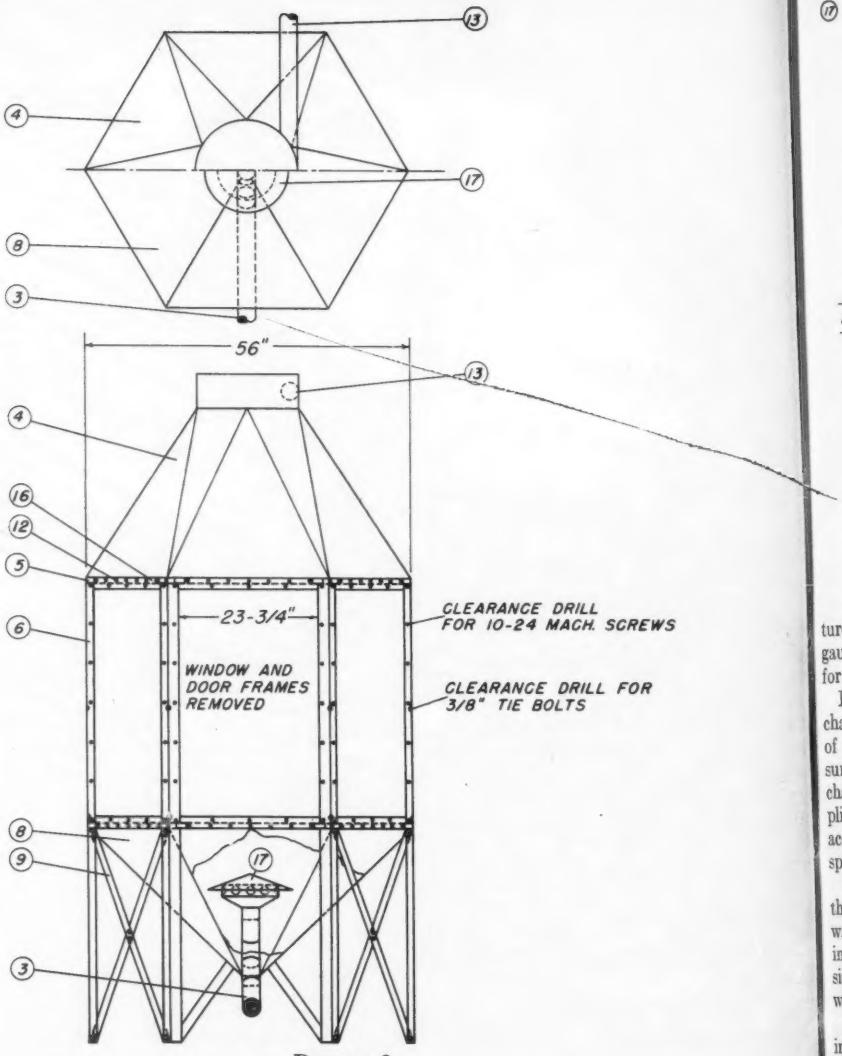
DRAWING 1.

during exposure. The lower level consists of a divided compartment which houses dogs separated according to sex.

Included in this report are drawings showing construction details and dimensions of the exposure chamber and its accessories. The circled reference numbers are listed in the materials table along with descriptive information.

Drawing No. 1 is an elevation and top view of the exposure chamber. Viewed from above the chamber is hexagonal in cross section with a dimension of 48 inches across the flats. The chamber top stands a little over nine feet above the floor level. The inlet air duct is shown at the top of the chamber; the exhaust air duct is at the bottom. Each chamber has two doors which swing outward for easy animal loading. Construction is of stainless steel with the exception of the windows; these are ¼-inch lucite panels.

In Drawing No. 2, also a top view and elevation, the chamber has been rotated 90° on its long axis toward the viewer. The cross sectional dimension in the top view, in this case, is about 56 inches. The cut-away portion in the lower cone of the chamber shows an apparatus used for filtering the exhaust air. It collects and retains animal hair and a good portion of the effluent UO_2 dust; these materials can cause operational difficulties in the pitot flowmeters mounted in the exhaust lines.



DRAWING 2.

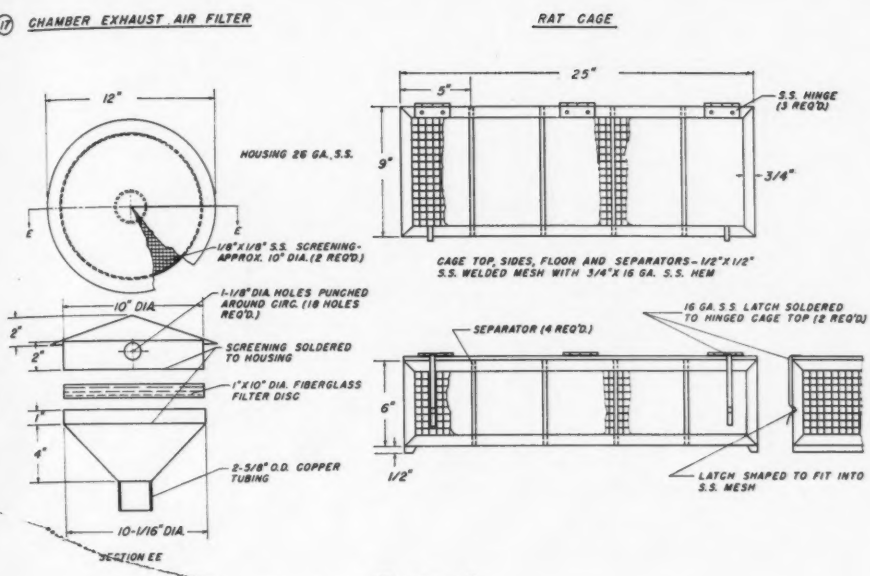
Drawing No. 3 shows the exhaust air filter more clearly. It consists of a stainless steel housing and a disposable fiberglass filter pad. Also shown in Drawing No. 3 are details of the rat cages. Each cage has generous space for five adult rats caged separately.

Construction details of the chamber doors and windows are shown in Drawing No. 4. The type and placement of the door hinges and closures can be seen in the photograph of the complete exposure unit (Figure 1).

Drawing No. 5 shows the rotating element which supports the monkey and rat cages. On the right are shown details of the monkey cages.

Drawing No. 6 shows the divided compartment which houses dogs separated according to sex, and on the right are some other construction details of the chamber.

Each chamber has its own air sampling and control meters. These are mounted on the master control panel. Included on our master panel are chamber air sampling meters, chamber tempera-



DRAWING 3.

ture gauges, chamber airflow and pressure gauges, and air pressure and electrical controls for the dust generator.

During normal operation, airflow through each chamber is balanced to maintain an airflow rate of 40 cubic feet per minute at a negative pressure of about 0.05 inch of water. Regulation of chamber airflow and static pressure is accomplished by manually adjusting control valves in accordance with prescribed settings on the respective gauges mounted on the control panel.

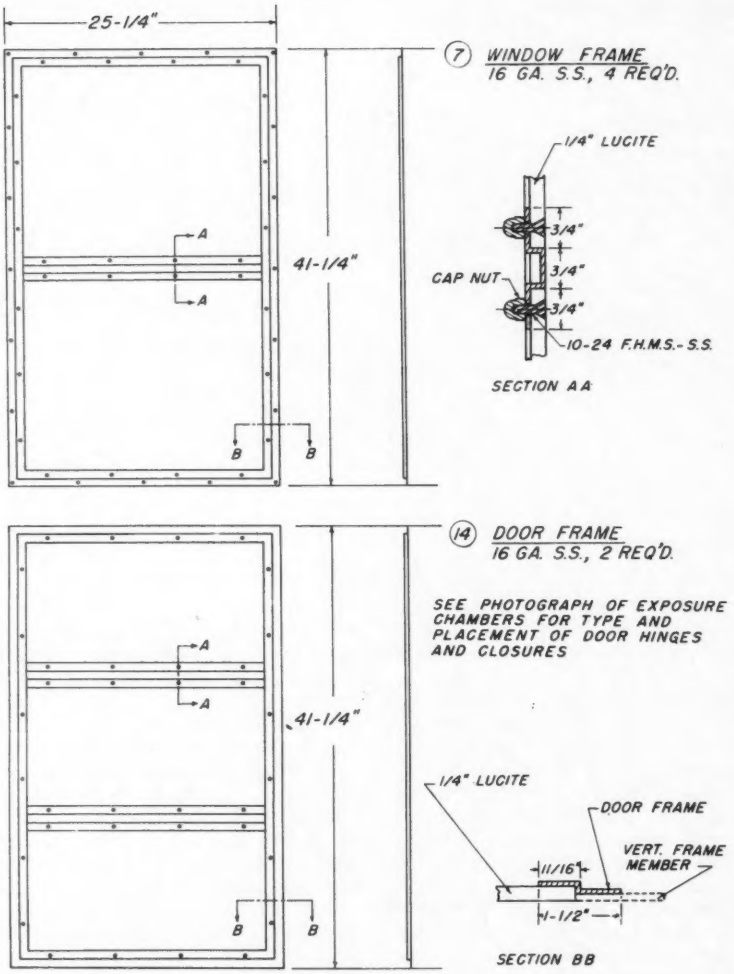
The uranium dioxide used in the testing of the chambers and later in the animal exposure was obtained from the Mallinckrodt Corporation in a 75-lb lot. To obtain the particle size considered suitable for the exposure study the dust was twice ground in a Bantam Mikro-pulverizer.

The pre-ground UO_2 dust is dispersed into the inlet air system of the exposure unit by means of the Wright Dust Feed Mechanism.[2] This is a British-made instrument which can be purchased from the L. Adams Co., Ltd., of London, England. A photograph of the dust generator is shown in Figure 3. In this view you can see the metal instrument frame (A), the electric clock motor drive (B), the changeable gear train (C), the dust tube (D) which contain the tightly packed test material, the compressed air inlet (E) and the outlet nozzle (F).

Figure 4 is a schematic drawing of the instrument in cross section. During operation the dust tube containing the compressed dust is rotated downward over a stationary circular scraper blade. The scrapings from the surface of the compressed dust are directed into a channel machined into the scraper head. Compressed air supplied to the instrument at the air inlet, travels up the hollow spindle, picks up the dust scrapings, and transports them back through the central air channel of the spindle and out the nozzle. The dust traveling through the nozzle is impacted on a plate in order to break up any agglomerates formed in the scraping process.

The concentration of airborne uranium dust within the chamber is determined by using filter paper dust samplers[3] attached to 12-inch probes. The method of sampling consists of collecting the dust from a known volume of chamber air on Whatman No. 41 filter paper disks. These disks are then analyzed for uranium (U) by the ferrocyanide method.[4] The dust concentration expressed in milligrams (mg) of U or of UO_2 per cubic meter (m^3) of air is then calculated from the amount of U deposited on the filter paper disks and the known volume of chamber air sampled. During the actual operation of the unit the chambers are sampled simultaneously over a fixed period at regular time intervals.

In the process of establishing the desired exposure conditions for the animal study, that is, a dust concentration level of 5 mg U/m^3 with a particle size of about one micron mass median

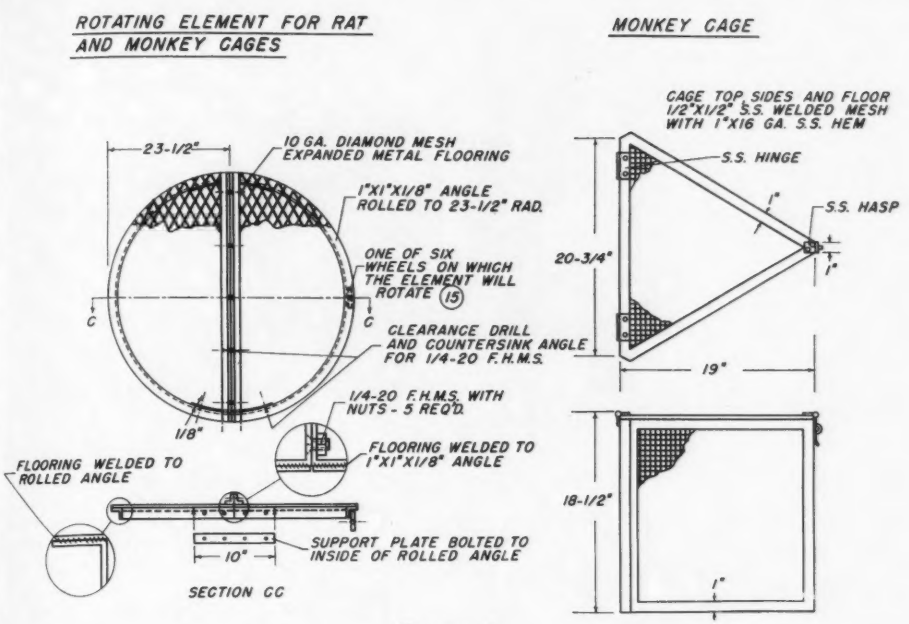


DRAWING 4.

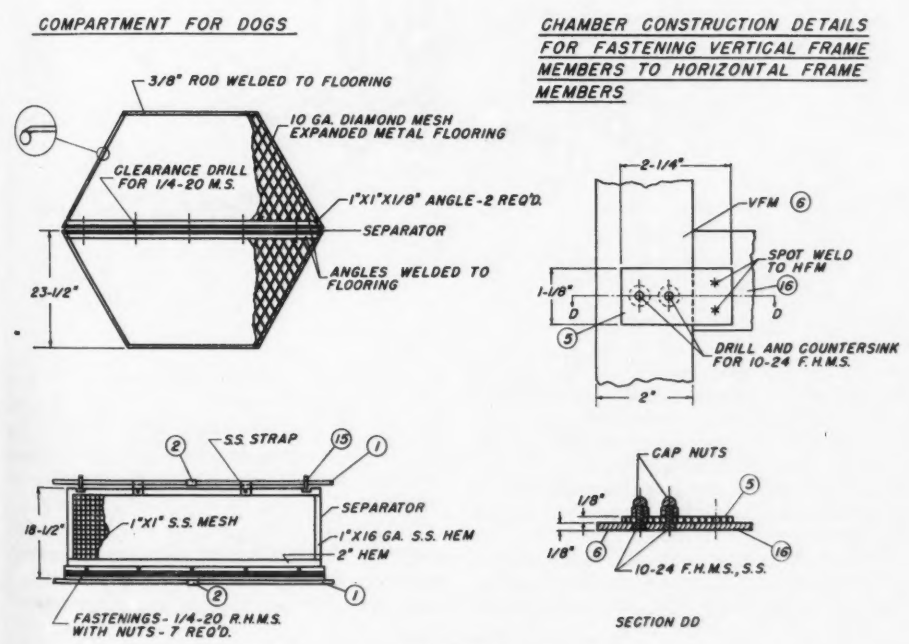
particle diameter (MMD), methods were developed to produce and maintain dusty atmospheres of uniform concentration and particle size. Because these procedures were involved and were repeated and modified until satisfactory results were obtained, they will not be fully described in this report. Only the results of one interesting study made during the testing of the chambers will be given.

To find the uniformity of dust concentration within each chamber, a distribution study was made employing the test dust at about 7 mg UO_2/m^3. Air samples were taken at twelve positions within each chamber. Three successively higher elevations designated as Port A, Port B and Port C, were investigated. Filter paper dust samplers having various probe lengths of from 6 to 24 inches were used in a sampling traverse of each elevation. To determine the variation in concentration between individual chambers, they were sampled simultaneously at each sampling position. The results of these tests are shown in Figure 5. Dust concentrations are expressed as percentages of those obtained at reference site R, which is the routine sampling position.

The mean dust concentrations varied from 85 to 101 percent of those obtained at the refer-



DRAWING 5.



DRAWING 6.

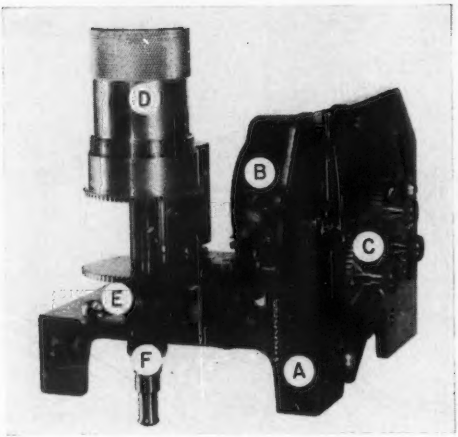


FIGURE 3.

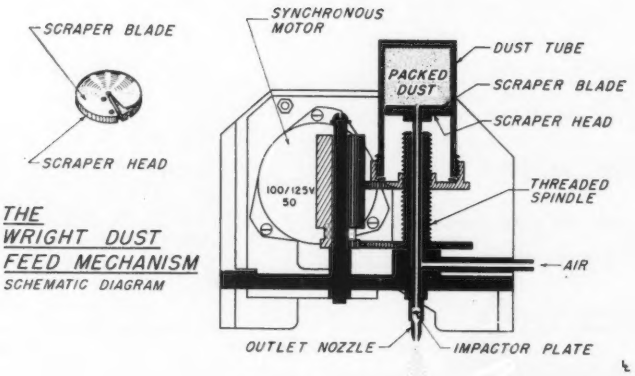


FIGURE 4.

ence site. If the data obtained at the 24-inch probe length are omitted (which can be justified by the fact that it is almost physically impossible to expose animals along the centerline of the chamber) then the over-all variation becomes only 7 per cent. In any case this study showed that the distribution of dust within the exposure chambers was satisfactory.

Table I shows the results of the statistical analysis of chamber dust concentration data obtained during the first two years of animal exposure. The mean dust concentrations for the four chambers ranged from 5.59 to 5.77 mg UO_2/m^3. The low value of 0.41 mg UO_2/m^3 obtained for the standard deviation indicates that atmospheres of reasonably uniform dust concentrations were maintained during the exposure period.

The results of four particle size studies made during the same 2-year exposure period are presented in Table II. The time interval between each sampling was approximately six months.

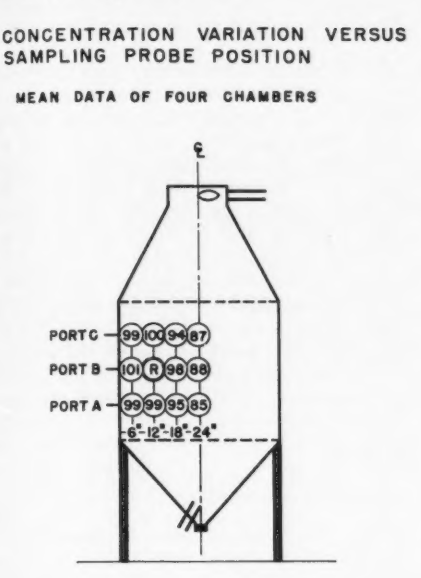

CONCENTRATION VARIATION VERSUS SAMPLING PROBE POSITION
MEAN DATA OF FOUR CHAMBERS
℄
PORT C
99 100 94 87
PORT B
101 R 98 88
PORT A
99 99 95 85
6" 12" 18" 24"
ASSUMING REFERENCE SITE (R) = 100% THEN THE EXTREME VARIATION IN DUST CONCENTRATION WAS 16 %.

FIGURE 5.

TABLE I

Statistical Analysis of Chamber Dust Concentration Data Obtained During the First Two Years of Animal Exposure

Chamber	No. of air samples analyzed	Mean dust concentration, mg UO_2/m^3	Standard deviation, (4 chambers) mg UO_2/m^3
1	481	5.59	0.41
2	482	5.77	
3	480	5.59	
4	481	5.69	

The size-mass distributions were obtained with a modified cascade impactor[3] and determined by chemical analysis.[4] Individual and mean values for the mass median particle diameter (MMD) and geometric standard deviation (σ_g) are given in the table. The mean mass median particle diameter values for the four chambers ranged from 0.95 to 0.98 microns. Mean values for the geometric standard deviation ranged from 2.47 to 2.61. The mean data shown in the table indicate that the atmospheres in each of the chambers were comparable in particle-size distributions.

TABLE II

Size-Mass Distribution of Uranium Dioxide Dust Occurring in the First Two Years of Animal Exposure*

Chamber No.	Sample No.	Chamber dust concentration, mg UO_2/m^3	Mass median particle diameter (MMD), microns	Geometric standard deviation (σ_g)
1	1		1.00	2.80
	2		0.96	2.83
	3		0.99	2.26
	4		0.97	2.56
	Mean	5.59	0.98	2.61
2	1		0.94	2.68
	2		0.92	2.60
	3		0.98	2.14
	4		0.95	2.45
	Mean	5.77	0.95	2.47
3	1		1.00	2.70
	2		0.91	2.57
	3		0.96	2.26
	4		0.96	2.56
	Mean	5.59	0.96	2.52
4	1		0.94	2.66
	2		1.02	2.84
	3		0.96	2.30
	4		1.01	2.43
	Mean	5.69	0.98	2.56

* Results obtained with a Modified Cascade Impactor[3] and determined by chemical analysis.[4]

Summary and Conclusions

1. To expose a relatively large number of animals for a 5-year long study of the inhalation of uranium dioxide, four separate chambers of the hexagonal type have been combined to operate from a common air intake and dust feed system.

2. The animal capacity of the new unit is 16 monkeys, 32 beagle dogs and 160 rats.

3. The exposure unit has been in operation for approximately 2½ years; performance has been satisfactory. The atmospheres in the four chambers are for most practical purposes, identical in dust concentration and particle-size distributions.

4. While the new unit was designed primarily for a long-term study with large numbers of animals, it may be modified easily for other types of inhalation experiments. By separate control of individual dust inlets, four different concentrations of the same compound or four different compounds could be tested simultaneously.

TABLE III

Materials of Construction

Item	No. Req'd.	Description
1	12	Tie Rods—3/8" D—Threaded on Each End—S.S.
2	2	Hex Blocks—2" x 1/2" Thick—Drilled and Tapped—S.S.
3	1	Exhaust Air Duct—2 1/2" I.D. Copper Tubing
4	1	Chamber Top Cone—1/8" Sheet S.S.
5	24	Fastening Plates—2 1/4" x 1 1/8" x 1/8" Thick S.S.—Dwg. No. 6
6	6	Vertical Frame Members—4" x 1/8" Thick S.S.
7	4	Window Frames—16 Ga. S.S.—Dwg. No. 4
8	1	Chamber Bottom Cone—1/8" Sheet S.S.
9	6	Vertical Frame Braces—2" x 1/4" Thick, S.S.
10	1	Waste Drain—3" I.D. x 3" S.S. Tubing
11	320*	Window Fastenings—10-24 F.H.M.S. with Cap Nuts, S. S.
12	175*	Chamber Cone Fastenings—10-24 R.H.M.S with Cap Nuts, S.S.
13	1	Supply Air Duct—2 1/2" I.D. Copper Tubing
14	2	Door Frames—16 Ga. S.S.—Dwg. No. 4
15	6	Wheels—2"D x 1/2" Thick—Brass, with Ball Bearing Race
16	12	Horizontal Frame Members—2" x 1/8" Thick, S.S.
17	1	Exhaust Air Filter Housing†—26 Ga. S.S.—Dwg. No. 3

* Approximate number.

† Housing contains 10"D x 1" Thick disc of ultrafine fiberglass No. 751, American Airfilter Co., Louisville 8, Kentucky.

Acknowledgments

The authors acknowledge with appreciation the suggestions and encouragement given by Dr. Harold C. Hodge and Dr. Elliott A. Maynard. Contributions were made by the following associates: Dr. Thomas Mercer, particle size consultant; Dr. Arthur Dutton, statistics; Leon Schwartz and staff, photography; Norman Oakes (supervisor), William Scott (master electrician), Frederick Graumenz (master mechanic), Clarence Fuller (master carpenter), installation of exposure equipment; and Raymond Kesel and staff, animal care.

To those who aided in other ways and are not cited individually, the authors take this opportunity to express their sincere gratitude.

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WHO KNOWS?

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The Determination of Thallium in Urine and Air*

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Introduction

THALLIUM has been measured by iodometric titration of the thallic ion or by polarography following dithizone separation of the thallium.[1] Our attention has been drawn to the appearance in the chemical literature of a number of organic reagents which seem to be relatively specific for thallium.[2] These reagents combine with complex thallium anions to form highly colored complexes soluble in organic solvents.

If the organic reagents (basic dyes) may be represented by R_3N, the chemical reactions involved are as follows:

$$Tl^{+} + Br_2 = Tl^{+++} \quad (1)$$

$$Tl^{+++} + 4Br^{-} = TlBr_4^{-} \quad (2)$$

$$TlBr_4^{-} + R_3NH^{+} = R_3NHTlBr_4 \quad (3)$$

The oxidation of the thallous ion to the thallic ion is most expeditiously carried out with free bromine since the excess is removed simply by boiling (Equation 1).

The thallic ion is apparently stabilized by formation of the tetrabromothallate anion (Equation 2). We postulate that the reaction of the basic dye (in acid solution) with the tetrabromothallate ion is that indicated in Equation 3. The large molecule formed is obviously unionized since it is readily extractable into solvents such as amyl acetate or toluene.

Table I lists basic dyes, some of which have been reported to react as described with thallium. Visual examination of the extracted color, developed under the conditions to be described, yielded the approximate estimates of sensitivity shown.

Methyl violet, crystal violet, brilliant green, malachite green, and rhodamine-B were the only materials tested which seemed promising. A number of related basic triphenylmethane dyes were useless for this work. We have selected methyl violet for our work with analytical absorption spectroscopy. Russian workers have indicated that crystal violet is superior to methyl violet; we have found, however, that our samples of methyl violet, crystal violet, or even gentian violet yield essentially the same results, not an unexpected development, since all three dyes are reported to be somewhat contaminated mixtures of approximately the same composition. The red thallium-rhodamine-B complex is highly fluorescent and forms the basis of a tremendously sensitive test; however, reproducible results could not be attained using rhodamine-B and the blanks were high and variable. As a consequence of these findings, all further work was carried out using methyl violet.

Reagents and Solutions

All chemicals used were reagent grade; organic chemicals used were Eastmen organic chemicals.

Sulfuric acid: 96 per cent, specific gravity 1.84

0.5*N* Sulfuric acid

Nitric acid: 70 per cent, specific gravity 1.42

Hydrobromic acid: (47 per cent HBr). The bromine usually present is not removed. Dilute hydrobromic acid is prepared by making a 1:10 dilution of the 47 per cent hydrobromic acid with distilled water.

Bromine: The bromine water used was prepared by saturating distilled water with bromine.

Perchloric acid: 70 to 72 per cent

n-Octyl alcohol

n-Amyl acetate

Methyl violet: EKC No. 1309. A stock 0.1 per cent methyl violet solution is prepared by dissolving 0.1 gm in distilled water. The working methyl violet solution is prepared by diluting (just prior to use) 5 ml of the stock methyl violet with 1 ml of 0.5*N* sulfuric acid and 4 ml of distilled water.

Thallium standard: Weigh out 1.303 gm thallium nitrate ($TlNO_3$), place in a one liter volumetric flask, and dilute to volume with 0.5*N* sulfuric acid. By serial dilution prepare a diluted thallium solution so that 1 ml = 1 μg thallium. (A fresh dilute solution should be prepared every two to three days.)

1:9 Sulfuric-nitric acid digestion mixture: Add

* This work was done under the auspices of the U. S. Atomic Energy Commission.

TABLE I

Reaction of Thallium with Selected Organic Reagents

Compound	Intensity of Color
Methyl violet	++++
Crystal violet	++++
Brilliant green	+++
Malachite green	+++
Rhodamine-B	+++
Safranine-O	+
Fuchsin	0

one volume of sulfuric acid to nine volumes of nitric acid.

1:1:8 Digestion mixture: To eight volumes of nitric acid add one volume of sulfuric acid and one volume of perchloric acid.

Boiling chips: Carborundum Brand, Silicon Carbide Grain; 20 grit.

Procedure

Digestion of Filter Paper Samples

Either the 1⅛-inch or 2⅛-inch filter papers are used to sample for thallium in air.

The filter papers are folded and placed in 90 ml round-bottom centrifuge tubes, and 5 ml of the 1:9 digestion mixture is added. The tube is then heated in a sand bath at 180°C until fumes of nitric acid are no longer seen or until the charred solution is not boiling. The tube is cooled, 2 ml of the 1:1:8 digestion mixture is added, and the tube is heated in a sand bath at 350°C until the solution is colorless and fumes of sulfuric trioxide are evolved. Copious fumes of sulfur trioxide must be seen prior to removal of the tube from the sand bath. The filter paper samples are now ready for the oxidation procedure.

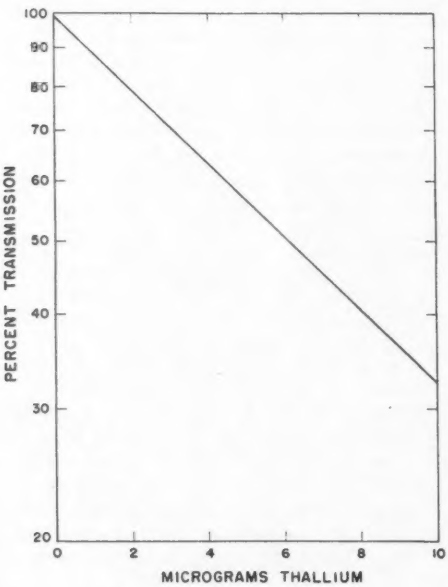

FIGURE 1. Standard Curve.

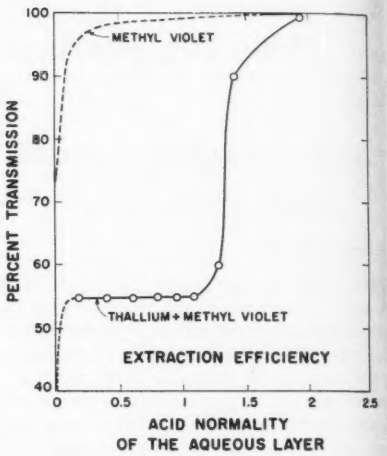

FIGURE 2. Extraction Efficiency.

Digestion of Urine Samples

Transfer 100 ml of urine to a 500 ml round-bottom flask, add boiling chips, 10 ml of 1:9 digestion mixture, and several drops of antifoam (*n*-octyl alcohol). Evaporate the urine to fumes of sulfur trioxide and cool; add nitric acid to aid in destruction of organic matter. Four to six drops of sulfuric acid must be added if the flask becomes dry during the process. When the residue is white and damp with sulfuric acid, the samples are ready for the oxidation procedure.

Preparation of Standards for Oxidation

To five 90 ml tubes add 0, 1, 2, 4, and 10 ml of the dilute thallium standard. To each tube add sufficient 0.5*N* sulfuric acid so that the total volume is 10 ml; the tubes then contain 0, 1, 2, 4, and 10 μg thallium, respectively. Add 5 ml of 1:9 digestion mixture and heat at 180°C until the solution no longer boils. Transfer to a 350°C sand bath and evaporate to fumes of sulfuric trioxide. Do not heat after fumes begin to evolve from the tube. The standards are now ready for the oxidation procedure.

Oxidation Procedure

Wash down the walls of the urine flasks, of the air sample tube, and of the standard tubes with distilled water to make the volume of each about 20 ml. Add one ml of 47 per cent hydrobromic acid and heat in a 180°C sand bath until the solution turns a light brown. (The standards will form only a fleeting tan which is easily seen.) The tube should be heated only until fumes of sulfur trioxide are just visible in the tube. Allow the flasks and tubes to cool, and again wash down the walls with distilled water to a volume of 20 ml; warm to dissolve all solids. Add one ml dilute hydrobromic acid and, if no free bromine is seen, add several drops of bromine water; place the solutions in a 180°C sand bath and boil until the solutions are clear and colorless, indicating removal of bromine. Without undue delay, transfer the solutions to 125 ml separatory funnels for extraction.

Extraction and Determination

Make the final volume of the solution in the separatory funnel to 50 to 75 ml with distilled water and allow the solutions to cool to room temperature. Add 10 ml *n*-amyl acetate to each funnel and one ml of the working methyl violet solution to one funnel; shake this funnel immediately for 10 to 15 seconds, continue with the addition of methyl violet to other funnels, and shake each as before. Finally, shake each funnel for an additional 45 to 50 seconds. When the layers have separated, discard the aqueous lower phase and drain the n-amyl acetate layer into a 15 ml centrifuge tube. Centrifuge the tubes to free the solution of water. Decant the blue-violet *n*-amyl acetate layer into matched cuvettes (Coleman 19 × 105 mm) and measure the per cent transmission at 585 millimicrons using pure *n*-amyl acetate as a reference. Determine the amount of thallium in the unknowns from a plot of the sandard curve on semilog paper (Figure 1).

Discussion

Recoveries of thallium added to blank, pooled urines average 96 ± 6 per cent. Examination of urines from unexposed personnel indicate the invariable presence of 0.1 to 0.2 micrograms of apparent thallium per 100 milliliters of urine. For highly reproducible results, it is necessary that technicians be intimately familiar with the procedural details, especially those indicated in the oxidation procedure.

The working methyl violet solution must be prepared as directed; the use of neutral or alkaline dye solutions leads to high blanks and erroneous results.

The removal of excess bromine after oxidation of thallium has been accomplished in the past with either phenol or sulfosalicylic acid. It has been our experience that the use of these reagents is not as satisfactory as the physical removal of excess bromine by vaporization. It has been indicated[3] that the oxidation of antimony to the pentavalent state can be brought about with nitrous acid, the excess being removed by urea. We have not been able to oxidize thallium quantitatively with nitrous acid under the conditions suggested.

Control of acid normality is imperative during the extraction. Figure 2 illustrates that the thallium-methyl violet complex is completely extracted from aqueous solutions 0.5 to 1*N* in mineral acid. At lower acidities, the free base (R_3N) is preferentially extracted by the organic solvent; at higher acidities, the complex is not formed. The presence in the aqueous phase of free phosphoric, nitric, or perchloric acids interferes with the extraction.

The thallium-methyl violet complex is very stable in the amyl acetate solution; it should not, however, be allowed to stand for protracted periods in contact with the aqueous acid from which it has been extracted. It is possible to extract the complex from acid solutions of normality as high as 1.5 with greatly lowered efficiency of extraction.

Summary

A method is described for the analysis of collected air samples or urine for thallium, with recoveries averaging 96 ± 6 per cent. Procedures are given for the preliminary preparation of samples for the preparation of the standard curve, for the oxidation of thallous ion to thallic ion, and for the extraction and measurement of the thallium-methyl violet complex. Comments pertinent to the development and use of the method are made.

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Estimation of Hydrazine and Three of Its Methyl Derivatives*

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Introduction

THE increasing industrial uses of hydrazine and its derivatives have stimulated studies of the health hazards associated with the manufacture and application of these compounds. This laboratory recently completed investigations[1] on the acute vapor toxicity of hydrazine, monomethylhydrazine, 1,1-dimethylhydrazine (asymmetrical), and 1,2-dimethylhydrazine (symmetrical). In this work, dispersed vapors of the agents were collected by absorption in water acidified with hydrochloric acid. Hydrazine concentrations were determined by potentiometric titration with potassium bromate[2]; concentrations of the methyl derivative were determined by titration with potassium iodate, using a visual end-point.[3] In another study[4], low vapor concentrations of hydrazine were estimated by a method based upon the reduction of phosphomolybdic acid by hydrazine to molybdenum blue, the color intensity being measured photometrically at 420 millimicrons.

It appeared of interest to compare and apply each of the above methods to the estimation of each of the hydrazines because of the general applicability of potentiometric methods to oxidation-reduction reactions and the general usefulness of colorimetric methods for the determination of very low concentrations. (In order to facilitate discussion, hydrazine and its three methyl derivatives will also be collectively referred to in this report as the "hydrazines" or "hydrazine bases".) This report describes the results obtained by application of three methods (i.e., visual iodate, potentiometric bromate, and colorimetric molybdenum blue) to the determination of hydrazine and its methyl derivatives. In addition, the validity of continuous sampling techniques for vapor concentrations in air was determined by estimating the stability of acidified aqueous solutions of the hydrazines toward prolonged aeration.

* Presented at the American Industrial Hygiene Association annual meeting on April 25, 1958, Atlantic City, New Jersey

Experimental Procedures and Results

Standardization of Salt Solutions

Salts of the hydrazines were used for analytical standards because of the well-known instability and hygroscopicity of the free bases. It was necessary to determine the hydrazine moiety in the salts by methods other than those under study. Hence, solutions of the salts were assayed by determining their acid radical content and calculating the equivalent of the corresponding hydrazine component.

The following salts were used in this work: hydrazine sulfate, methylhydrazine sulfate, s-dimethylhydrazine dihydrochloride, and as-dimethylhydrazine oxalate. The sulfates were standardized gravimetrically by barium sulfate precipitation. The dihydrochloride was standardized by determination of the chloride content using the Volhard procedure. The oxalate was standardized by titration with potassium permanganate after removal of the hydrazine by distillation from alkaline solution. A summary of some data on the salts is shown in Table I.

In studies with as-dimethylhydrazine oxalate it was necessary to check the possibility of interference of the oxalate radical in the reaction between the reagents and the hydrazine. Oxalate-free standards were prepared as follows: solutions of the oxalate were made strongly alkaline with sodium hydroxide and the liberated hydrazine was quantitatively distilled into water acidified with hydrochloric acid. This solution was then standardized by the method under study and the results compared with those obtained when the salt was used directly.

The Potassium Iodate Titration

Known volumes of standard solutions of the hydrazine salts were analyzed by the Jamieson method[3] as follows: the solution was made strongly acid by the addition of concentrated HCl. A few ml of chloroform were added and the solution was titrated in an ice bath with 0.1*M* potassium iodate, using a micro-burette. The

TABLE I

Summary of Data on Salts Used as Standards

Compound	Salt	Formula	Mol. Wt.	Melting Point, °C.		Method of standardization
				Observed	Literature	
Hydrazine	Sulfate[a]	$NH_2NH_2 \cdot H_2SO_4$	130.1	244–5	254	Gravimetric – $BaSO_4$
Methylhydrazine	Sulfate[b]	$CH_3NHNH_2 \cdot H_2SO_4$	144.2	142–3	141–2	Gravimetric – $BaSO_4$
as-Dimethylhydrazine	Oxalate[c]	$(CH_3)_2NNH_2 \cdot H_2C_2O_4$	150.1	146–7	142–3	Volumetric – $KMnO_4$
s-Dimethylhydrazine	Dihydrochloride[d]	$CH_3NHNHCH_3 \cdot 2\ HCl$	133.0	160–2	165–7	Volumetric– $AgNO_3$ + KCNS

(a) J. T. Baker's C. P. grade.
(b) Eastman's white label grade.
(c) Supplied by the Metalectro Corporation, Laurel, Md.
(d) Synthesized in this laboratory.

TABLE II

Determination of Hydrazine Derivatives with Potassium Iodate

Compound	Quantity taken		No. of Detns.	Exptl. mean value for electron change	Assumed rational values for the reaction		
	Salt	Hydrazine			Electron change	Equiv. Wt. / Mol. Wt.	Molar reaction ratio, KIO_3: compound
	mg	mg					
Hydrazine	58.9	14.5	4	3.97	4	1/4	1:1
Methylhydrazine	50.0	16.0	4	4.03	4	1/4	1:1
as-Dimethylhydrazine	52.6	21.1	4	2.00	2	1/2	1:2
sym-Dimethylhydrazine	43.0	19.4	4	5.75	6	1/6	3:2

disappearance of the iodine color from the chloroform layer was taken as the end-point of the titration. Results are shown in Table II.

The electron change of the hydrazine molecule in this reaction was calculated by use of the following formula[5]:

$$\begin{bmatrix}\text{electron change of the hydrazine}\end{bmatrix} = \frac{\begin{bmatrix}\text{volume of } KIO_3\end{bmatrix} \times \begin{bmatrix}\text{molarity of } KIO_3\end{bmatrix} \times \begin{bmatrix}\text{electron change of } KIO_3\end{bmatrix} \times \begin{bmatrix}\text{molecular weight of salt}\end{bmatrix}}{1000 \times [\text{weight of salt in grams}]}$$

As an example, in the titration of hydrazine sulfate substitution of experimental data in the formula gives:

$$\text{electron change} = \frac{(4.493) \times (0.1) \times (4)(130.12)}{(1000) \times (0.0589)} = 3.97$$

The electron change of the KIO_3 molecule is known from the fact that in this titration the pentavalent iodine of KIO_3 is reduced to iodine monochloride, in which compound its valence is plus one. Hence, the electron change of the KIO_3 is four. The equivalent weight of hydrazine in this reaction is thus apparent from the value of its electron change, i.e., one-fourth of its molecular weight. Equating the electronic changes also shows that hydrazine reacts mole for mole with KIO_3.

The oxalate radical did not interfere in the reaction between potassium iodate and as-dimethylhydrazine. This was shown by the following facts: (a) potassium iodate did not react with oxalic acid nor sodium oxalate in the cold, although it is known that iodate oxidizes oxalic acid rapidly in hot solutions; (b) oxalate-free solutions of as-dimethylhydrazine gave results similar to those shown in Table II.

The Potentiometric Potassium Bromate Titration

To known volumes of standard solutions of the hydrazine salts were added 20 ml of concentrated HCl and 2 gm of potassium bromide. The resulting solutions were titrated potentiometrically with $M/60$ potassium bromate, using a

TABLE III

DETERMINATION OF HYDRAZINE DERIVATIVES WITH POTASSIUM BROMATE

Compound	Quantity taken		No. of Detns.	Exptl. mean value for electron change	Assumed rational values for the reaction		
	Salt	Hydrazine			Electron change	Equiv. Wt. / Mol. Wt.	Molar reaction ratio, $KBrO_3$: compound
	mg	mg					
Hydrazine	12.4	3.05	3	4.05	4	1/4	2:3
Methylhydrazine	10.0	3.2	5	3.97	4	1/4	2:3
s-Dimethylhydrazine	10.8	4.86	5	5.85	6	1/6	1:1

micro-burette and a Beckman Model G pH meter equipped with calomel and platinum electrodes. The equivalence point was calculated by the method described by Kolthoff and Sandell.[6] Results are shown in Table III.

In this titration, the pentavalent bromine of $KBrO_3$ is reduced to KBr, in which compound its valence is minus one. Hence, the electron change of the $KBrO_3$ is six. The electron changes, equivalent weight, and molar reaction ratio of each hydrazine were determined by the methods described above.

Results obtained with as-dimethylhydrazine are not shown in Table III because the end-point of the reaction varied with the rate of addition of the reagent and was not reproducible. The oxalate radical did not cause this since oxalate-free solutions of as-dimethylhydrazine showed the same behavior.

"Recoveries" of each hydrazine by the KIO_3 and $KBrO_3$ titrations were determined by calculating the quantity found using the rational equivalent weight and dividing this quantity by the amount of pure hydrazine taken for analysis. Results are summarized in Table IV.

TABLE IV

Recovery of Hydrazine Derivatives by the Potassium Iodate and Potassium Bromate Methods

Compound	Average wt. hydrazine taken	Average wt. hydrazine found	No. of detns.	Average recovery
	mg	mg		%
Method: KIO_3 titration				
Hydrazine	14.5	14.4	4	99.3
Methylhydrazine	16.0	16.1	4	100.6
as-Dimethylhydrazine	21.1	21.1	4	100.0
s-Dimethylhydrazine	19.4	18.6	4	95.9
Method: $KBrO_3$ titration				
Hydrazine	3.05	3.08	3	101.0
Methylhydrazine	3.20	3.18	5	99.4
s-Dimethylhydrazine	4.86	4.74	5	97.5

The Colorimetric Molybdenum Blue Method

Two ml of phosphomolybdic acid reagent[7] were added to known volumes of standard solutions of the hydrazine salts contained in graduated Klett cuvettes, and the mixtures were diluted to ca. 8 ml. The solutions and a reagent blank were heated for exactly 15 minutes in a water bath maintained at 98.0 ± 0.2°C and then cooled to room temperature by immersion in cold running water. The solutions were made up to the 10 ml mark with water. The intensity of the developed color was measured in a Klett-Summerson photoelectric colorimeter using a blue filter (420 millimicrons). The net colorimeter readings were plotted against the quantities of the hydrazines to give the standard curves shown in Figure 1. Data are given in Table V.

Results obtained with as-dimethylhydrazine are not shown in Figure 1 or Table V because a linear standard curve was not obtained under these conditions. The oxalate radical did not cause this since oxalate-free solutions of the hydrazine showed the same behavior.

Because of the importance of as-dimethylhydrazine and the hope that the cause of the lack of linearity might be readily discovered, further investigation of this method was undertaken. First, a study of the effect of length of heating upon color formation was made, using two standard solutions of different strengths. Results are shown in Table VI.

The data in Table VI show that practically maximum color development is attained at 45 minutes in the case of the stronger standard and at 25 minutes in the case of the weaker standard. However, since no serious deterioration in color intensity of the weaker standard occurred as a result of heating it for 50 minutes, and to provide a margin for slight variations in conditions in case of the stronger standard, a heating time of 50 minutes was adopted as the optimum.

The reproducibility and linearity of the curve using the 50-minute heating period was next

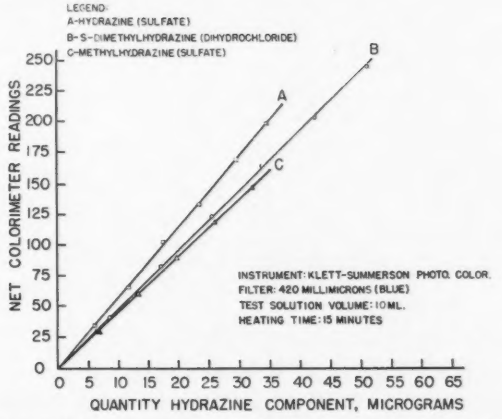

FIG. 1. Colorimetric determination of hydrazines by molybdenum blue method.

TABLE V

Colorimetric Determination of Hydrazine Derivatives by Molydenum Blue Method

Compound	Quantity taken	Net Klett readings	Sensitivity*
	micrograms		
Hydrazine	5.8	35	6.0
	11.6	68	5.9
	17.4	102	5.9
	23.2	133	5.7
	29.0	168	5.8
	34.8	199	5.7
			5.8 Mean
Methylhydrazine	6.4	30	4.7
	12.8	59	4.6
	19.2	89	4.6
	25.6	120	4.7
	32.0	150	4.7
			4.7 Mean
s-Dimethylhydrazine	8.5	42	4.9
	17.0	85	5.0
	25.4	123	4.8
	33.9	167	4.9
	42.4	201	4.7
	50.9	241	4.7
			4.9 Mean

* Sensitivity = $\frac{\text{net Klett readings}}{\text{micrograms compound}}$

The mean sensitivity is equal to the slope since

Slope = b = $\frac{\text{Sum Y (readings)}}{\text{Sum X (quantities)}}$

TABLE VI

Effect of Heating Time upon Formation of Molybdenum Blue in the Colorimetric Analysis of as-Dimethylhydrazine

Quantity compound present: 48.9 micrograms		Quantity compound present: 24.5 micrograms	
Heating period	Klett readings*	Heating period	Klett readings*
mins		mins	
15	177	15	130
20	207	20	139
25	231	25	147
30	246	30	149
35	268	35	145
40	280	40	148
45	288	45	151
50	290	50	148
60	291	55	148
		60	145

* Klett readings not corrected by a blank.

determined. Five curves were prepared on different days, using from 4 to 45 micrograms of as-dimethylhydrazine. The slopes of these curves were 5.0, 5.0, 5.0, 4.8, and 5.1 respectively. A composite standard curve with slope of 5.0 was constructed by averaging the Klett readings for each concentration and is shown in Figure 2.

Comparison of Analytical Methods

Aqueous solutions of commercial grade, free hydrazine bases were acidified with a slight excess of HCl. Hydrazine and methylhydrazine solutions were also acidified with a slight excess

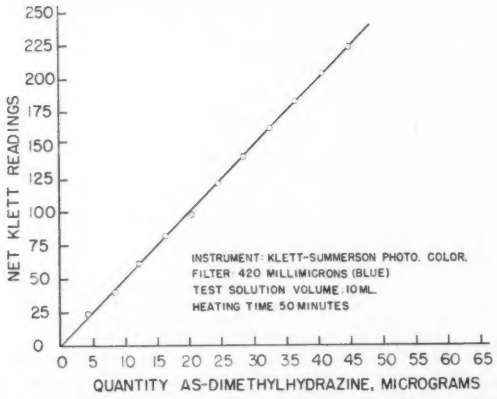

FIG. 2. Colorimetric determination of as-dimethylhydrazine by molybdenum blue method.

TABLE VII

Comparison of Results Obtained by Application of Three Analytical Methods to Aerated and Non-aerated Acidified Solutions of Hydrazine and Its Methylated Derivatives

Solution	Method of analysis	Concentration of solution		Stability
		Before aeration	After aeration	
		mg/ml	mg/ml	%
Hydrazine + H_2SO_4	KIO_3	0.95	0.95	100
	$KBrO_3$	0.96	0.96	100
	CMB*	0.92	0.92	100
Hydrazine + HCl	CMB**	0.30	0.30	100
Methylhydrazine + H_2SO_4	KIO_3	0.95	0.95	100
	$KBrO_3$	0.94	0.94	100
	CMB*	0.95	0.94	98.9
Methylhydrazine + HCl	CMB**	0.21	0.20	95.2
as-Dimethylhydrazine + HCl	KIO_3	1.11	1.11	100
	$KBrO_3$	—	—	—
	CMB*	1.09	1.11	101.8
s-Dimethylhydrazine + HCl	KIO_3	—	—	—
	$KBrO_3$	1.20	1.20	100
	CMB*	1.19	1.20	100.8

* CMB is symbol for the colorimetric molybdenum blue method. Concentrations calculated by reference to simultaneously analyzed standard hydrazine salt solutions.

** Concentrations calculated by reference to original standard curve (Figure 1).

of sulfuric acid. Each solution was assayed by the visual iodate, the potentiometric bromate, and the colorimetric molybdenum blue methods, with the exceptions shown in Table VII. Next, 25 ml. of each solution were placed in Vigreaux-type absorption tubes and aerated for 30 minutes at a rate of 0.5 liter of air per minute. The solutions were then assayed again by the same methods. The results obtained by each method and the stability (percentage recovery) are shown in Table VII.

Discussion

The experimental data show that all the hydrazines may be satisfactorily determined by potassium iodate titration although comparatively less accurate results are obtained with s-dimethylhydrazine. The potentiometric bromate titration is applicable to the determination of every hydrazine, except as-dimethylhydrazine. The reasons for this exception are not apparent, but it is probable that variations in the rate of reaction with the reagent or the existence of complicating side reactions are responsible.

The data in Table V and the standard curves in Figure 1 and 2 show good conformity with the Beer-Lambert law. Although the optimum experimental conditions for the colorimetric analysis, such as heating time, reagent concentration, etc., were not determined for each hydrazine, the accuracy of the method under the experimental conditions described is good. This is shown by the good agreement of the colorimetric results with those obtained by the KIO_3 and $KBrO_3$ titration methods (Table VII).

In the case of as-dimethylhydrazine, the study of the effect of heating time upon color formation proved to be of value, since an optimum heating period—50 minutes—was developed, which yielded a standard curve of good reproducibility and linearity (Figure 2).

The data in Table VII show that if vapors of the hydrazines are collected in acid solution by continuous sampling methods no significant loss of compound by oxidation or aeration should occur. Table VII also shows good agreement among the results obtained by application of

the three analytical methods to the determination of the hydrazines in both aerated and non-aerated acidified solutions.

If it is assumed that a 10-liter sample is drawn from a chamber and absorbed in 25 ml of acidified water, and that a 5 ml aliquot of this solution is analyzed, then the lowest chamber concentrations determinable by the molybdenum blue method would be approximately 3 micrograms/liter for hydrazine and methylhydrazine, (2.3 and 1.6 ppm respectively) and 4 micrograms/liter (1.6 ppm) for as-dimethylhydrazine and s-dimethylhydrazine. The sensitivity of the method should make it possible to determine even lower vapor concentrations provided that suitable adjustments of sampling conditions are made.

It might appear from the data in Table II and III that the potassium iodate and potassium bromate methods would be suitable only for the determination of vapor concentrations of the order of a few milligrams per liter. However, the quantities of the compounds taken for analysis were certainly arbitrary, and there is no doubt that smaller amounts could be satisfactorily analyzed and, hence, lower vapor concentrations determined by these methods.

Conclusions

Milligram quantities of hydrazine, methylhydrazine, s-dimethylhydrazine, and as-dimethylhydrazine can be satisfactorily determined in acid aqueous solution by the Jamieson potassium iodate titration. These hydrazines, except for as-dimethylhydrazine, can also be satisfactorily analyzed by potentiometric titration with potassium bromate. A colorimetric molybdenum blue procedure is suitable for the determination of microgram quantities of these compounds.

All four hydrazines in acid solution are stable toward aeration for at least 30 minutes, indicating that continuous sampling techniques may be used for determining vapor concentrations of these compounds in air.

Vapor concentrations of these compounds ranging from several micrograms to several milligrams per liter can be accurately and rapidly determinable by application of the appropriate method.

Acknowledgments

The advice of Mr. Francis P. McGrath in writing this report and the assistance of Pvt. John M. Boyles in carrying out some of the analyses are gratefully acknowledged.

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Conference on Gaseous and Industrial Wastes

A UNIQUE CONFERENCE DEALING with solids separation from gaseous and liquid wastes will be held at Hotel Traymore, Atlantic City, New Jersey on March 10 and 11, 1959. The first day's session, sponsored by the Mid-Atlantic States Section of the Air Pollution Control Association, will consider problems of gaseous wastes. The program of the second day will deal with liquid wastes and interrelationships with gaseous wastes, and will be presented by the Industrial Wastes Committee of the New Jersey Sewage and Industrial Wastes Association.

This conference will offer an opportunity to persons interested in pollution problems to obtain a complete and integrated view of such problems and their solutions. The separate direction of each session by an organization specifically interested and qualified in that area will insure a high calibre program. Such a venture will also encourage cooperative thought and stimulate exchange of information for the solution of industrial waste problems.

Determination of Tributylphosphine in Air

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THE production of tributylphosphine in commercial quantities requires that the industrial hygienist be prepared to determine concentrations of this material in air, as a means of safeguarding the health of the workers exposed to this compound.

Tributylphosphine or the products of its reaction with oxygen in air can be determined through the phosphorus present in the molecule. Collection of air samples by a cold-surface trap is the most successful of the methods tried. Oxidation of the organo-phosphorus to orthophosphate is accomplished in the trap by oxidation with potassium dichromate for 15 minutes at 180°C. A digestion period of 15 minutes at 100°C is necessary before 100 per cent recovery of phosphorus can be obtained. The phosphorus as orthophosphate is reacted with ammonium molybdate at a controlled pH and extracted into butanol as ammonium molybdiphosphate.[1] The ammonium molybdiphosphate is reduced in the butanol phase with stannous chloride to form the "molybdenum blué" complex.[2] The procedure described will detect one microgram of phosphorus in the aliquot analyzed and can be used to determine tributylphosphine concentrations in air as low as one part per million by volume.

Analytical Method

Sampling Procedure

A cold-surface trap is employed for the collection of air samples (Figure 1). Effective collection is dependent on a limited sampling rate. At a sampling rate of 50 cc/min, 90% efficiency was obtained. At sampling rates of 100 and 500 cc/min, efficiencies of 70% and 50%, respectively, were obtained. Therefore, one trap is used at 50 cc/min, two traps in series at 100 cc/min and three traps in series at 500 cc/min.

The trap is immersed in a dry ice-acetone slush, and the volume of air drawn through the trap is metered accurately. The volume of air sampled should be two to five liters, if possible. When low concentration of tributylphosphine (TBP) are expected (0 to 1 ppm), a 5-liter or larger sample should be taken. If the expected concentration is 5 to 10 ppm, a one-liter sample can be taken and analyzed with good reliability.

Sample Preparation

Allow the trap to warm up to room temperature and introduce 10 ml of the oxidizing solution through the delivery tube (Reagent C). Close both stopcocks and place the trap in mineral oil at 180°C for 15 minutes. Remove the trap and cool it to room temperature. Place the trap on a steam bath at 100°C for 15 minutes. Remove the trap, cool it to room temperature, and wash the contents into a 100-ml volumetric flask using distilled water sparingly (10 ml or less). Add cautiously 10 to 12 ml of methanol to destroy excess dichromate ion. Complete reaction may require 20 to 30 minutes. Color of the reduced solution should be deep blue. Dilute to the mark with distilled water. Prepare a reagent blank in the manner just described.

Reagents

(A) Ammonium molybdate, 5 per cent. Add 10 mg of reagent grade ammonium molybdate to a 200-ml volumetric flask containing 100 ml of distilled water. Dissolve and dilute to the mark with distilled water.

(B) Butanol, Union Carbide Chemicals Company, commercial grade.

(C) Oxidizing mixture. To 50 ml of a saturated aqueous (distilled water) solution of reagent grade potassium dichromate, add 100 ml of concentrated sulfuric acid slowly and with constant stirring. Allow to cool to room temperature before using. (*NOTE:* Excess potassium dichromate will precipitate out of the solution on cooling. Shake to suspend the potassium dichromate and pipet immediately.)

(D) Sulfuric acid, reagent grade, concentrated.

(E) Sulfuric acid, 1*N*. Dilute 28 ml of concentrated sulfuric acid to one liter with distilled water.

(F) Sulfuric acid, 0.5*N*. Dilute 14 ml of con-

centrated sulfuric acid to one liter with distilled water.

(G) Ammonium hydroxide, reagent grade, phosphate free.

(H) Stannous chloride, stock solution. Dissolve 10 gm in 25 ml of concentrated hydrochloric acid. (Stable for 10 days only.)

(I) Stannous chloride, reducing solution. Dilute 4 ml of stock solution to 100 ml using 0.5 *N* sulfuric acid.

(J) Standard phosphate solution. Dissolve 1 gm of dry dibasic sodium phosphate in 0.5*N* sulfuric acid and dilute to one liter with additional acid. Dilute 10 ml of this solution to one liter with 0.5*N* sulfuric acid. One ml contains 2.18 micrograms of phosphorus.

Procedure

Pipet 25 ml of the sample, or an aliquot containing less than 40 micrograms of phosphorus, and a like volume of the reagent blank into separate 100-ml beakers. Using a pH meter, adjust the pH of the solutions to exactly 1.25 by the addition of small increments of concentrated ammonium hydroxide. Do not allow the temperature of the solutions to rise above room temperature or 28°C during this operation or low results will be encountered. Transfer the solutions to separate 125-ml graduated separatory funnels. Rinse the beakers with small portions of 0.5*N* sulfuric acid, and add the rinsings to the funnels. Dilute the contents to 40 ± 0.5 ml with additional acid. Using suitable pipets, add 2 ml of ammonium molybdate reagent and 15 ml of butanol to each funnel. Stopper and shake each funnel 50 times. Allow the layers to separate. Remove and discard the lower layer. Into each funnel pipet 5 ml of 0.5*N* sulfuric acid and mix by shaking 10 to 15 times. Allow the layers to separate and discard the lower layer. Repeat the washing step just described to insure complete removal of excess ammonium molybdate reagent. Into each funnel, pipet 5 ml of the stannous chloride reducing solution. Mix by shaking for exactly one minute. Let stand for exactly two minutes and discard the lower layer. Into each funnel, pipet 5 ml of 1.0 *N* sulfuric acid. Mix by shaking 10 to 15 times. Allow layers to separate and discard lower layer. Pipet 10 ml of the butanol layers to respective 25-ml glass-stoppered graduates and dilute to 20 ml with methanol. Shake the graduates to mix and to insure the solution of any water droplets present. Transfer the sample and blank to 1-cm cells for the Beckman Model B spectrophotometer and obtain the absorbance for the sample at a wavelength of 730 millimicrons based on a reading of zero for the blank. From a previously prepared calibration curve, read the micrograms of phosphorus corresponding to the absorbance.

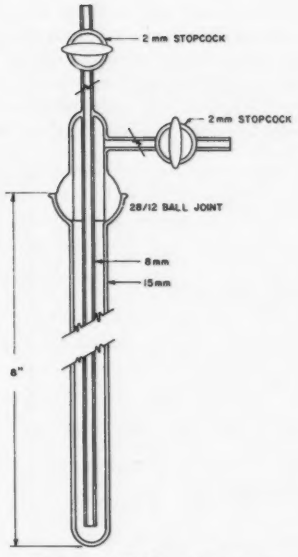

FIGURE 1. Cold-surface trap.

Calibration Curve

Using the standard phosphate solution listed under reagents, pipet 0, 5, 10, and 15 milliliters of the 2.18 micrograms P/ml solution into graduated separatory funnels. Adjust the volume to 40.0 ± 0.5 milliliters with 0.5*N* sulfuric acid. Develop the color by the procedure as described. Plot the absorbance versus the micrograms of phosphorus.

Calculation

The concentration as ppm by volume tributylphosphine (TBP) gas in air may be calculated by use of the following equation:

$$\text{ppm TBP} = \frac{\text{total P} \times \text{gm-mole-vol}}{30.98 \times \text{sample volume}}$$

where—total P is expressed in micrograms of phosphorus,
—gm-mole-vol is the gram molecular volume in liters at 25°C and 760 mm Hg,
—30.98 is the atomic weight of phosphorus,
—sample volume is the liters of air sampled corrected to 25°C and 760 mm Hg.

Several steps in the method must be performed cautiously to insure personnel safety and phosphorus recovery. The oxidizing solution should be added through the delivery tube to wash the TBP into the main body of the cold trap shown in Figure 1. When heating the sample to 180°C, the analyst should adequately shield the mineral oil bath because pressures of about 150 psi within the trap may be encountered. Leakage of vapor at the stopcocks during this step was encountered with no serious effect on the phosphorus recovery. When reducing the excess dichromate ion, methanol reacts vigorously with the oxidant and can be flashed if it is not added carefully. After the excess dichromate is destroyed, the color of the solution will be deep blue. High results may be encountered if there is any dichromate ion remaining in the solution.

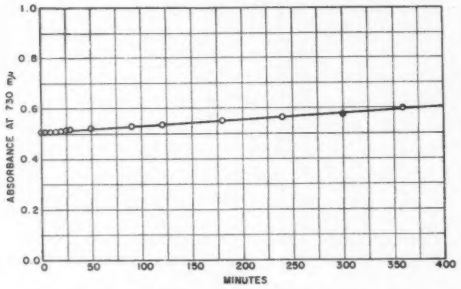

FIGURE 2. Stability of "molybdenum blue" complex in butanol.

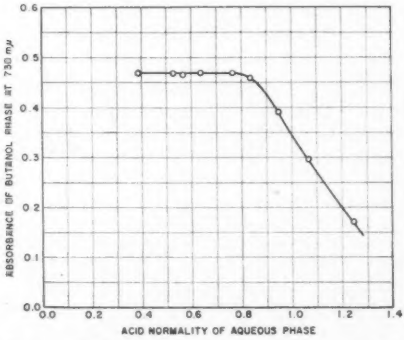

FIGURE 3. Extraction of ammonium molybdiphosphate into butanol from aqueous solution.

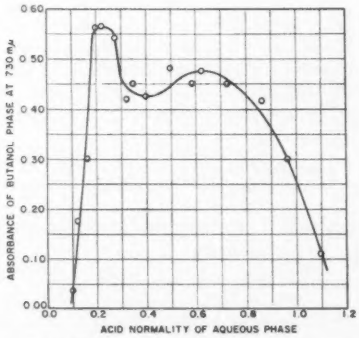

FIGURE 4. Extraction of ammonium molybdiphosphate into butanol from aqueous solution of dichromate ion.

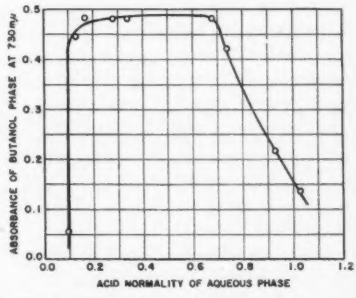

FIGURE 5. Extraction of ammonium molybdiphosphate into butanol from aqueous solution of chromic sulfate.

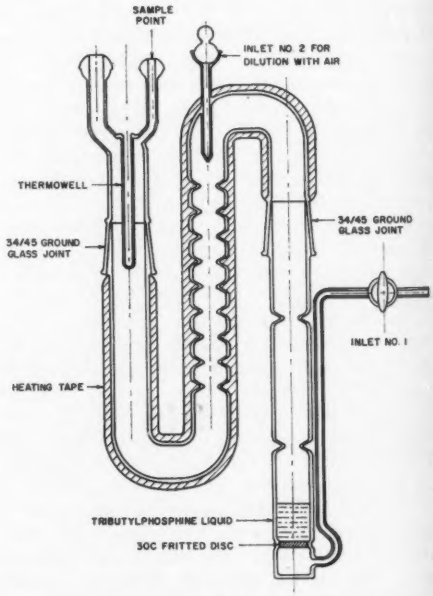

FIGURE 6. Apparatus for preparation of known concentrations of tributylphosphine in gases.

An important feature in the preparation of the sample for extraction with butanol is control of the temperature during adjustment of pH. Control of the maximum temperature of the sample to room temperature is generally adequate, but an upper limit of about 28°C probably should be maintained.

Discussion

Extraction of the sample with butanol and development of the color is accomplished easily. With different volumes of sample, the volume of butanol recovered will vary. For this reason, a fraction of the recovered butanol (10 ml) is diluted to 20 ml with methanol.

The "molybdenum blue" complex generally has the stability illustrated by the data in Figure 2. The stability indicated is normal, but samples should be read immediately since, for reasons unknown, the color will occasionally fade out, after standing for a short period of time.

Extraction of Ammonium Molybdiphosphate into Butanol

To determine the optimum normality for extraction of ammonium molybdiphosphate into butanol, extractions were performed at various normalities on a solution containing a known quantity of orthophosphate (Figure 3). Extractions of the same phosphate solution were also performed in the presence of excess dichromate ion (Figure 4) and reduced dichromate ion (chromic sulfate) (Figure 5). The extraction of the ammonium molybdiphosphate proceeded best at an acid normality of 0.3 to 0.7. Recovery of phosphate from the solutions containing dichromate and chromic ions was good, but recovery was more reliable where the dichromate ions had been reduced to chromic sulfate by the addition of small quantities of methanol.

Preparation of Known Concentrations of Tributylphosphine in Gases

A. Nitrogen. Numerous attempts to prepare samples of TBP vapor in nitrogen resulted in failure. It was felt, with some certainty, that the TBP vapor was condensing out of the nitrogen before it reached the sample point. This view was supported by the presence of tiny droplets of TBP observed in the dilution chamber after the system had been operating for two or three days at room temperature. Because of this, the temperature of the system (Figure 6) was elevated to 40°C immediately following exposure of nitrogen to the liquid TBP. The portion of the system containing TBP liquid was maintained at room temperature.

Table I

Preparation of Known Concentrations of Tributylphosphine in Air

Sample No.	Flow rate (cc/min)		ppm TBP (by chemical analysis)	Expected ppm TBP (by dilution)
	Nitrogen	Air		
1	50	—	35.9	
2	50	—	32.7	
3	50	—	37.2	
4	50	—	34.6	
5	50	50	18.7	16 to 18
6	50	50	15.7	16 to 18
7	50	50	17.2	16 to 18
8	50	100	14.2	12 to 14
9	50	100	15.0	12 to 14
10	50	100	13.5	12 to 14
11	50	950	1.5	1 to 2
12	50	950	1.3	1 to 2
13	50	950	1.4	1 to 2
14	50	950	1.6	1 to 2
15	50	950	1.6	1 to 2
16	50	950	1.8	1 to 2
17	50	950	1.9	1 to 2
18	50	950	1.8	1 to 2

During the first attempts to prepare a known concentration of TBP in nitrogen, the assumption was made that in passing through the vaporizer the nitrogen stream was saturated with TBP. This assumption permitted calculations of concentrations based on vapor pressure. Consistently low results by chemical analyses and an indirect relationship between actual concentrations and the nitrogen flow rate indicate that a partial saturation of nitrogen with TBP was actually obtained.

B. Air. Using the system as previously described, the nitrogen stream was diluted with air to simulate samples that would exist in air contaminated with TBP. The retention time of the TBP with air was two to three minutes due to the size of the dilution chamber. The wall temperature in the dilution chamber was elevated to 200 to 230°C to insure against condensation of TBP and its oxygenated products. Table I gives the results of the chemical analyses of samples taken from the air stream. Variations in the concentrations of TBP are attributed to the variations in the wall temperature of the mixing chamber. However, concentrations agree with those predicted based on the dilution ratio.

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New Developments in Oxygen Deficiency Testing*

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Introduction

VERY soon after the discovery of oxygen and clarification of its physiological significance, it was learned that breathing air with less than the normal O_2 content of 20.8% by volume is detrimental to the well being of man and that exposure to air containing less than 16% O_2 will rapidly cause unconsciousness and if prolonged will be fatal. Ever since this became known, the need for a simple and reliable method and instrument for testing the oxygen content of the surrounding atmosphere was realized. But strange as it may seem, progress in this field has been slow—and even in our atomic and space age when many physical quantities are being measured daily with accuracies of a part in a million and some even in parts per billion, it is still not an easy job to ascertain the oxygen content of a gas mixture by laboratory procedures with an accuracy of better than 0.05% O_2 or 1 part in 400 at 20%. Direct indicating instruments even of the most expensive continuous types with an accuracy better than 1% full scale or 0.2% O_2 near 20% are still in the offing. There are two main reasons for this: oxygen is always all around us, indeed we live in an ocean of air containing a high percentage of oxygen; oxygen is not only chemically reactive with many materials, but is in addition strongly ad- and absorbed by very many liquids and by solids, which are used for vessels, pipes, etc. and released again when temperature or pressure is changed.

Existing Methods

The oldest device for oxygen deficiency determination is the flame safety lamp. Almost since its inception, at the beginning of the nineteenth century, it was used in coal mines not only as a source of light but also as a detector of methane and of oxygen deficiency. However, so far as oxygen deficiency is concerned, this device never could be considered to be an "instrument", inasmuch as the only more or less definite observation that can be made with it is that the flame will go out when the O_2 concentration falls below approximately 16%. But even this is the case only when methane is absent; in the presence of methane, according to data of the U. S. Bureau of Mines[1], a flame safety lamp can continue to burn down to 13% O_2. In the range between normal air (20.8%) and the extinction point, the flame first increases in height, then, if methane is absent, decreases, but if methane is present, the flame elongates all the time with decrease of oxygen until it is extinguished. It is evident, therefore, that without the simultaneous use of a methane detector, it is impossible even to estimate with any degree of certainty how much below the normal the O_2 content is. In spite of this, while the flame safety lamp is at present used scarcely anywhere as a source of light, it is still, to this date, almost the only device used in mines for testing purposes.

Many attempts have been made to adapt the flame safety lamp for oxygen deficiency testing in other places than mines, such as in manholes of gas and electric distribution systems, prior to entering various storage tanks after steaming or flushing them with inert gas for removal of combustibles, in shipholds, etc. In spite of much effort and ingenuity spent on this, there is no flame lamp in existence which is really anywhere near safe for taking into an atmosphere that contains acetylene, hydrogen, manufactured gas, or even petroleum vapors. There are, however, some special lamps in use, especially in the gas industry, for testing of manholes for oxygen deficiency from the outside. The sample is brought to the flame by means of an aspirator bulb through a hose line, which at some intermediate place contains a flashback arrester. Only the flashback arrester which prevents propagation of flame and explosion back to the source of samples is what makes this device safe. The customer is warned not to take this lamp at any time into an atmosphere containing combustible gases or vapors.

Quantitative determination of oxygen in the atmosphere in the laboratory (as most members of this audience probably know) is carried out by chemisorption of the oxygen in various

* Presented at the American Industrial Hygiene Association annual meeting on April 24, 1958, Atlantic City, New Jersey

liquids such as pyrogallol, chromic salt solution, etc. Either the pressure is kept constant and the volume decrease measured, using such well known volumetric apparatus as the Orsat or Haldane, or the volume is kept constant and the change in pressure is measured. The accuracy, with which oxygen concentration can be measured by such apparatus in routine tests is $\pm 0.1\%$ O_2; when extreme care is being taken by an experienced and skillful analyst to avoid or compensate for complications due to absorption and dissolution, and desorption and evaporation of O_2 in and from the various liquids employed and by the tubing, stopcocks and other parts of the apparatus, an accuracy of $\pm .05\%$ O_2 can be obtained. However, considering the added sources of error introduced by taking a sample even in the special sampling bottles used for this purpose and transferring them to the laboratory and the analyzer, it is very doubtful that overall accuracies better than to $\pm .1\%$ O_2 have ever been obtained by this procedure.

There have been brought out several models of oxygen analysis apparatus simplified and made portable to make it possible to take them inside mines, or to manholes of gas systems. In the last few years, two devices working on the basis of measuring pressure changes at substantially constant volume with a diaphragm type manometer have appeared on the market, which might be called instruments inasmuch as oxygen content after a number of prescribed operations is read directly on a precalibrated scale. However, these instruments in addition to low accuracy are not free from the one shortcoming common to all absorption types apparatus which is merely time consuming and inconvenient in the laboratory but is quite aggravating when it happens in the field: there is no telling when the absorbing fluid is coming to the end of its capacity and replacing it in the field causes not only a delay, but under many conditions creates quite a hardship.

In the field of industrial testing for oxygen in flue gases, in steel making and in other metallurgical and chemical process control instrumentation, a number of instruments were and still are used which are based on providing an excess of a combustible gas or vapor, e.g. hydrogen or alcohol vapor, and burning it by means of a hot wire filament or of a catalyst. In view of the need for a supply of a combustible gas, these instruments are basically not suited for portable use. Nevertheless one, so called, portable instrument of this kind was put out some time ago by a well known oil company and extensively used in steel mills and for testing of automobile engine performance: by generating the hydrogen in an electrolytic cell incorporated in the instrument itself, "portability" was achieved—if an instrument weighing 30–40 pounds can be called "portable". In addition, obviously, these instruments need a lot of additional devices, when required to be anywhere near safe for use in or near explosive atmospheres. However, this instrument, as well as others of this type, as far as is known, except for some trials in submarines, was never used for oxygen *deficiency* testing, because much greater amounts of combustible material would be required than for testing of the 1–2% normally encountered in combustion and process control, or dilution of the test sample with nitrogen with a high degree of constancy would be needed.

Magnetic Methods

In the 1930's, methods for determination of oxygen based on its magnetic properties were proposed in Germany and developed to the stage of laboratory instruments. All substances with respect to their behavior in a magnetic field fall in one of two classes: they are either paramagnetic or diamagnetic. A paramegnetic substance offers less reluctance to passage of magnetic flux (or magnetic lines of force) than does a vacuum, and is said to have a positive volume susceptibility, k, and a magnetic permeability, μ, greater than one; the exact connection between these two quantities is:

$$\mu = 1 + 4\pi k$$

Diamagnetic materials have negative susceptibilities and, hence, their permeability μ is less than unity, that is lower than that of a vacuum.

A paramagnetic substance when placed between or near the poles of a magnet will tend to move into a place where the field is strongest; a diamagnetic material will tend to move out of the space between the poles and in general away from the stronger field into a region of weaker field strength.

The magnetic susceptibilities of most materials except iron, nickel, cobalt, and other ferromagnetic materials are very small quantities—of the order 10^{-6} or parts per billion. Nevertheless they were determined quite accurately by physicists of the nineteenth and the early part of our century by various ingenious methods. One of the methods used by the French scientist Curie consisted of suspending a rod carrying a small hollow glass sphere by means of a fine wire or a quartz fiber in the manner of a torsion balance similar to those used for studying of

the Coulomb forces. A nonuniform magnetic field is used, and it was established that the torsional force exerted upon the glass sphere is proportional both to the magnetic field and to the gradient of the magnetic field. The magnetic susceptibility of oxygen is positive and much larger than that of nearly all other gases, but even so the volume susceptibility of O_2 is only equal to $+141 \times 10^{-9}$ in cgs units, while the susceptibility of most other gases is negative and varies between -0.08 for He and -1.77×10^{-9} (for chlorine) and that of the only other paramagnetic gas NO is 61×10^{-9}.

When in 1940 our military forces announced the urgent need for an oxygen measuring instrument, Dr. Linus Pauling and his collaborators[2] decided to make use of this outstanding physical property of oxygen and after a while succeeded in overcoming the difficulties connected with measuring in the field the small quantities involved and in developing an instrument which proved useful for many practical applications. This instrument has been manufactured since the war in several models for continuous indication and recording as well as for spot testing. Figure 1 shows a schematic view of such an instrument in its simplest form: Permanent magnets provide strong magnetic fields between two pairs of pole tips. Suspended on a quartz fiber between the pole tips is a dumbbell-shaped test body consisting of two small hollow glass spheres. The gas to be analyzed surrounds the test body. Depending upon the difference between the magnetic susceptibilities of the glass spheres and the gas which the spheres displace, the test body is subjected to a magnetic force which causes it to rotate in or out of the magnetic field until it reaches an equilibrium position, when the magnetic rotational force is exactly balanced by the torsional restoring force of the quartz fiber. In the portable models a beam of light produced by a small flashlight bulb (fed by two dry cells) incorporated in the instrument is reflected from a small mirror on the test body and indicates the equilibrium position of the test body on a translucent scale calibrated in partial pressures or volume concentrations of oxygen.

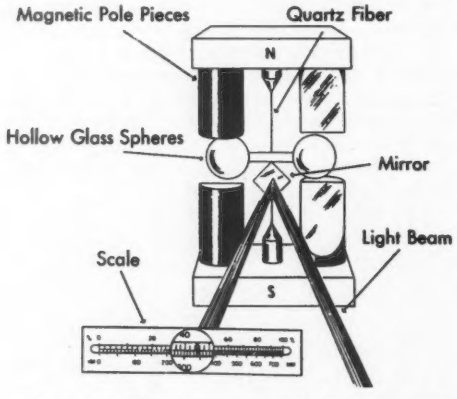

FIGURE 1. Schematic view showing how movement of test body suspended in a magnetic field causes light beam to indicate oxygen concentration on the scale.

The great advantage of this instrument, obviously, is its great simplicity of operation, and the apparently small amount of maintenance required. There are, however, a number of serious items on the opposite side of the ledger. The torsional forces produced in the instrument are extremely small: a 1% change in O_2 concentration produces a change in torsion of about 10^{-3} dyne $\times$ cm or about 1/1000 of a milligram $\times$ cm and thus in an instrument of this type having a 0–1% O_2 range the torsional force available is only 1/10,000 of the one used in the most sensitive recording galvanometer; even an instrument with a 0 to 25% O_2 range has available a deflecting force, which is only 1/400 of that of a highly sensitive galvanometer. Thus it is understandable why in the early instruments of this kind, breakage of the suspension was a quite frequent occurrence; and even now with the availability of stronger and lighter magnets of good constancy which has permitted the use of stronger suspensions, portable instruments of the paramagnetic type for the lower oxygen ranges are not quite satisfactory.

Because the sensitivity is directly proportional not only to the magnetic field strength but also to the gradient of the magnetic field, the position of the dumbbells in the field must also be maintained constant at all times with the greatest accuracy. This, in connection with the relatively low strength of the quartz fiber, makes the instrument position-sensitive: a tilt of the instrument by only 10° from the horizontal will produce an error, that exceeds the claimed accuracy of $\pm 2\%$ of scale range or 0.5% of O_2 on a 0 to 25% O_2 scale.

This reason as well as the fact that the indication is obtained on a vertical scale which must be held not much lower than eye level makes the instrument unsuitable for testing while being worn on a strap.

In the 0 to 1% range and to some extent in the 0–5% range, the effect of CO_2 when present in concentrations of 15 to 20%, as in flue gases, is so large that the oxygen readings without simultaneous CO_2 determination becomes quite illu-

sory. For these ranges also effects of temperature and surrounding magnetic fields make themselves felt. However, for oxygen deficiency determinations these effects seldom are significant.

Another type of instruments uses indirectly the high paramagnetic susceptibility of oxygen by observing the change of susceptibility with temperature which was first investigated by Curie. According to the Curie law, when a gas is heated, its volume magnetic susceptibility decreases in inverse proportion to the square of the absolute temperature. Therefore, when the gas is placed in a strong magnetic field, convection currents or a kind of magnetic wind is set up; the direction of the gas movement depends upon whether the gas is paramagnetic or diamagnetic, and the magnitude upon the magnitude of the magnetic susceptibility, upon the magnetic field strength and its gradient and upon the temperature and its gradient. The gas is heated by placing an electrically heated filament either inside the gas container or outside around a part of a small tube of good heat conductivity containing the gas under test; and it is the cooling produced by the magnetic wind as compared with the cooling in the absence of magnetic field or with the cooling of a substance of very low magnetic susceptibility in the same magnetic field which finally serves as a measure of the oxygen concentration.

This scheme, primarily developed in Germany by Senftleben[3] and his coworkers[4], paradoxical as it may seem in view of the many variable factors involved, is the basis of one of the most popular permanently mounted instruments for oxygen control in industrial establishments in Germany and in other countries.

Figure 2 shows a schematic diagram of one type of such instruments which enjoys great popularity in Germany. The basic principles of operation of an instrument using the Curie effect, which is very popular in this country, are illustrated in Figure 3. An instrument developed by Luft[5] instead of using the cooling produced by the magnetic wind measures the pressure variations, when the gas motion is restricted and the magnetic field is alternated by means of rotating pole pieces.

All instruments of this type have found only very limited application in the field of oxygen deficiency testing. This is because they do not lend themselves to development into a portable instrument: not only the weight and size of the batteries and strong magnets required are an obstacle, but, most of all, their inherent very great position dependence. Everybody who has observed the convection currents above a flame or above a radiator when made visible by the sun shining on them knows how little it takes to disturb them. The convention currents in these detectors are no exception: they are very easily disturbed by tilting of the instrument, and this of course greatly influences the cooling which is the measure of oxygen content.

The cooling and therefore the O_2 indication is also greatly influenced by presence in the mixture of CO_2, H_2, methane, city gas, and other gases, greatly differing from air in their molecular weight or in thermoconductivity. This influence, when the interfering gas is present in concentrations comparable with the oxygen content and these concentrations are subject to considerable variations, makes this kind of instrument for oxygen concentrations below 5% and

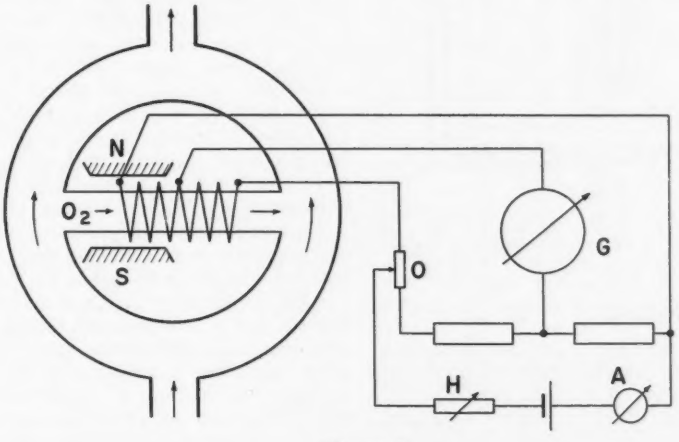

FIGURE 2.

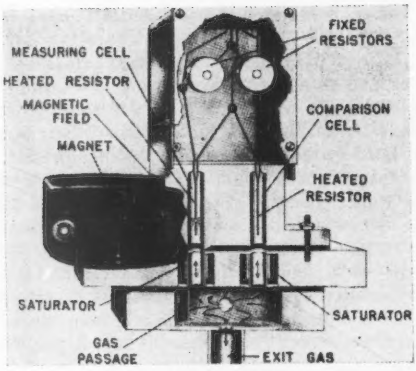

FIGURE 3.

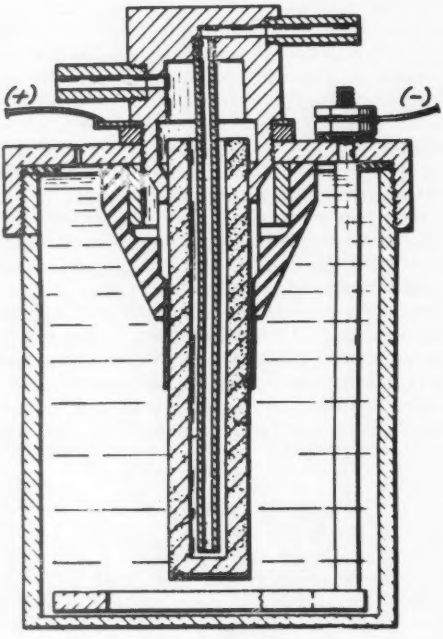

FIGURE 4.

for small differences of concentrations at higher oxygen levels quite inaccurate.

Electrochemical Methods

Electrochemical effects of oxygen have been known for a long time: a galvanic cell producing an electric potential and current was developed by Grove in 1839. Platinum electrodes enclosed in glass tubes were partly submerged in an acid electrolyte and the space around the electrodes

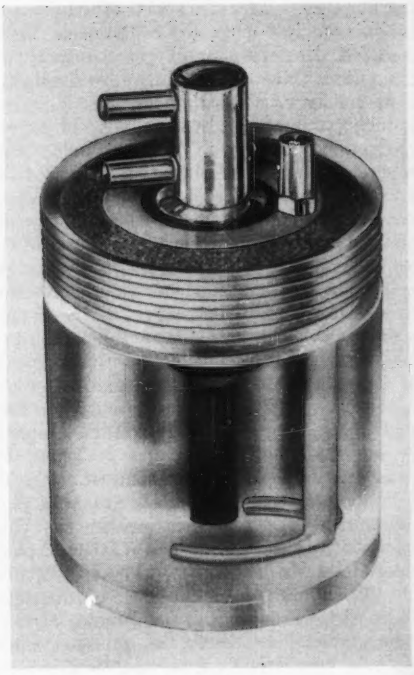

FIGURE 5.

above the electrolyte subjected respectively to flowing oxygen and hydrogen; a terminal voltage of slightly over 1 volt was obtained. This and similar gas cells were extensively investigated in laboratories, and considerable experimental and theoretical knowledge of their operation was accumulated. But to our knowledge, this direct electrochemical effect has not led to a successful development of a practical instrument for oxygen determination.

Another electrochemical effect, that of the redox (reduction-oxidation) potential, has been the subject of various attempts to develop an instrument for oxygen determination. These attempts while justly considered promising for determination of dissolved oxygen, scarcely will ever be successful for measurement of oxygen in gas mixtures, because of the time consuming process of dissolving the gas in the liquid, which is needed in the customary embodiments of this method, and also because of the many strong interferences by other components of the atmosphere. However, a modification of the redox method was developed successfully by the M.S.A. Company into a Continuous O_2 Recorder, which for many years rendered good service to numerous users.[6]

A copper ring is half immersed in an electrolyte, which has the property of reducing copper oxides to metallic copper. This ring is rotated by a motor and the clean copper surface when contacted by a gas mixture containing oxygen introduced above the surface of the electrolyte is oxidized in proportion to the O_2 concentration in the mixtures. When this oxidized part traverses the electrolyte, it not only gets reduced but produces an electromotive force, which is a measure of the oxygen concentration.

This instrument has very good operational characteristics, but requires a great deal of maintenance in replacing the electrolyte and removing interfering CO_2.

For some time it has been known that oxygen has definite halfwave potentials in the region between −0.1 and −1.0 volt, which greatly interfere with the potentiometric determination of various chemical substances by the dropping mercury electrode, rotating platinum and other potentiometric techniques. A great deal of time and effort is spent in these techniques to remove dissolved oxygen from the solution under test by bubbling nitrogen through it. Numerous attempts have been made to develop an oxygen measuring instrument by this method. While some of these appear promising so far as measurement of dissolved oxygen is concerned, it scarcely can be expected that any of these will become practical for measurement of gaseous oxygen.

The oxygen instruments developed and manufactured by the M.S.A. Company use an electrochemical method, which is quite different from any of the others. The detection and determination of oxygen is carried out by means of a galvanic cell in which the oxygen of the test gas acts as a depolarizer at the cathode. Everybody is familiar with the so called dry cells used as flashlight batteries which consist of a Zn anode and a carbon cathode immersed in a paste or jellylike electrolyte which contains ammonium chloride with various additives plus a depolarizer of manganese dioxide around the cathode. The process taking place inside the dry cell, when electric current is delivered, consists in positively charged hydrogen ions traveling to the cathode and negative ions traveling to the anode. In the absence of a depolarizer, the hydrogen ions would rapidly build up an opposing potential at the cathode; the manganese dioxide combining with the hydrogen ions prevents this and thus keeps the Electromotive Force and the current output substantially constant. At the beginning of this century a number of galvanic cells appeared in which the cathode was made of porous carbon and the oxygen from the surrounding atmosphere was used for depolarization, thus entirely avoiding the use of manganese dioxide. The French Fery cell is the best known of these, and various modifications of it are used abroad and in this country up to this day. Shortly after the appearance of these cells, A. Paris[7] in France suggested the use of a cell of this kind for quantitative determination of oxygen in gas mixtures. A. S. Moysseef and N. M. Brickman[8] in Russia further developed and investigated the use of this cell as a laboratory apparatus.

When at the beginning of the war the urgent need of a lightweight portable oxygen indicator became evident, research on this method of oxygen detection was started at the M.S.A. Laboratory. A portable indicator was developed which worked well in the laboratory but was not satisfactory for such applications as in submarines or on airplanes: the main shortcomings were a strong effect of temperature, which was still about 1% per 1°C after the M.S.A. Laboratory had cut it down from 1.8%, and influence of CO_2 and other acid gases. However, since the effect of temperature could be easily eliminated by thermostating, the method appeared promising for a continuous oxygen indicator for process control and other industrial applications, inasmuch as it required less maintenance than the M.S.A. redox type oxygen recorder. Consequently, a continuous O_2 analyzer using the depolarization method was developed, which was subjected to extensive field tests during 1944 and 1945 and put on the market in 1947. Subsequently further research on this method substantially eliminated the effect of CO_2 in concentrations up to 25%. This was accomplished by changing to an acid electrolyte in place of the alkaline electrolyte universally used in this cell before, and by keeping the cell current below a predetermined small value. Also the importance of the current density and the proper size of the active carbon surface was learned in our studies, and led to the development of a single uniform scale for all oxygen ranges, in place of the formerly necessary special calibration. These and other improvements were incorporated in the M.S.A. Model C-2 which was put on the market in 1952 and described in a paper presented by the senior author of this paper at the Pittsburgh Conference of Analytical Chemistry and Applied Spectroscopy.[9]

The significant improvements of the M.S.A. circuit consist in decreasing the detector cell current not by means of high resistance, but by opposing to it a current derived from an auxiliary source, such as a dry cell, and in so adjusting the total current output of the cell with

relation to the active carbon area that the current density per one per cent of oxygen remains constant. By this means not only is the detector cell current decreased, but at the same time the cell is operated at a higher and more constant terminal voltage. The practical result of this is that the slowing down of the response, which would be produced by the use of high resistance, is avoided, and that straight line calibration can be approached without significant drift.

In 1955 a model of this analyzer and recorder with automatic correction of drift and temperature influences every two, four, or eight hours was introduced by the M.S.A. Company. This instrument will give an accuracy of better than ±2% of the fullscale range, with very little service and maintenance, and is available in the ranges of 0 to 25%, 0 to 10%, 0 to 5%, and 0 to 1% O_2. CO_2 up to 25%, and hydrogen, methane, CO, and most other gases in concentrations up to 100% are of no influence.

When after ten years of research in connection with the continuous oxygen analyzer, the M.S.A. Laboratory returned to the task of developing a portable oxygen indicator, a considerable amount of knowledge and experience had accumulated. This made it possible to develop an instrument which is satisfactory not only for laboratory use but for most severe field applications.

In accomplishing this task, one of the first important developments was a completely new construction of the detector cell and of the electrodes. This is shown on Figures 4 and 5. The cell now has a solid bottom, thus completely eliminating the possibility of any leakage of the liquid electrolyte without the use of any gaskets, etc. Liquid electrolyte, rather than a paste or jelly, is used because with the latter the fast response which is now of the order of ⅓ second cannot be obtained.

The electrode of the portable analyzer is a carbon tube ¼ inch in oustide diameter by 2⅛ inches long, with an I.D. of about ⅛ inch, closed at the bottom. Part of the outside of this tube and the bottom are covered with an insulating paint, leaving a free carbon surface of about ½ to ¾ inch near the closed end, and about ½ inch near the open end. These carbon electrodes are carefully processed with a special waterproofing solution and several baking procedures. All of them are individually tested to very close mechanical and electrical tolerances. As a result of the electrical test, each electrode is tagged with two numerical parameters: (1) the zero setting; (2) the "check" setting. These are characteristic of the voltage from the auxiliary dry cell to be used with it, when inserted in any of the Portable Oxygen Indicators. After the instrument is adjusted to these two characteristics, indications within ±0.5% oxygen on the instrument scale are assured. Each instrument is individually tested and adjusted on a special simulator which is an electrical network that reproduces all important characteristics of an average detector cell.

The cuplike rubber boot or protector fits with its lower opening tightly over the carbon electrode, and with its wider cuplike part over a ring-shaped extension of the top of the cell. The object of this cup is twofold: (a) to prevent electrolyte from reaching the metal parts of the electrode holder; and (b) to prevent any gas from penetrating to the electrolyte by any other route except through the pores of the carbon and the interface of the carbon and electrolyte.

The carbon electrode makes contact and is held by a metal holder with four spring contact prongs. The holder also has a fine metal tube which extends inside of the carbon electrode and serves as an inlet for the gas mixture being tested. The mixture emerges near the closed bottom of the carbon electrode, then returns between the outside wall of the metal tube and the inside wall of the carbon electrode. Part of the sample, a very small quantity indeed, penetrates by diffusion through the pores of the carbon to the interface with the electrolyte, where O_2 if present reacts with the hydrogen ions to produce an E.M.F. in accordance with the O_2 concentration. Hydrogen and other molecules and atoms in the gas mixture which are not ionized do not have any eletrochemical effect. Insertion and removal of an electrode in the Portable Oxygen Indicator is just as easy as replacement of a radio tube or any other plug-in part.

It should be noted that now a single dry cell is used instead of the three in the continuous oxygen analyzer; the circuit is so designed that this single cell carries out all three functions: (1) provides a source for the bucking current; (2) a source for the zero adjustment—to correct for small current remnants with no oxygen present; (3) a source for improvement of drift and temperature effects. The useful life of the dry cell is almost equal to its shelf life.

An entirely novel feature is the "check" arrangement: by means of a double pole double throw switch and a high resistance in series, the O_2 indicating meter is temporarily used as a voltmeter to measure and adjust the voltage across a certain part of the circuit to a value predetermined and indicated for the particular carbon electrode in use, which will produce an electric current output in proportion to the square of the O_2 concentrations. The only other adjust-

ment needed preceding a series of tests is adjustment of the current output with atmospheric air as a sample to 20.8% on the scale (corresponding in the present model to a current burden of about 75 microamperes). Figure 6 shows a general view of the instrument.

A square root scale was chosen for the meter for the following reasons:

(1) A square root relationship provides the smallest variation with O_2 concentration of the internal electrical resistance of the detector cell.

(2) In consequence of this, the temperature coefficient is also reduced.

(3) Better readability and possibility of higher accuracy at the lower concentrations is obtained. For example: in the region of 2 to 4% oxygen often it is desirable to know the O_2 concentration better than to 0.5%. The square root scale in this range can be read to 0.2%, and with a little additional care an accuracy of $\pm 0.2\%$ O_2 in this range can be obtained.

The operation of this instrument by the user is as follows:

After the instrument is switched on by means of the switch on the upper right of the panel, the switch on the lower right is momentarily thrown to the "check" position and the pointer adjusted by means of the Check Adj. control to whatever check reading is indicated for the carbon electrode presently in use. This check reading usually is shown on a sticker attached to the Check Adj. knob.

Atmospheric air is aspirated and the pointer by means of the Air Adj. control is adjusted to 20.8% O_2. After a warmup time of 5 minutes, the Air Adj. is rechecked and readjusted, if needed, and the instrument is ready for testing of a sample with unknown oxygen content.

With a 5-foot sampling line, when the oxygen concentration is different from air, after 2–3 aspirations the pointer begins to move and in about 30–50 seconds reaches about 90% of its ultimate deflection. In 50–90 seconds it reaches its final stable position; the exact response time depends on the age of the electrode and electrolyte and other factors. The response time of the detector electrode itself is ⅓ of a second or less. Three interruptions per second of sample flow are still distinctly reproduced in movements of the meter pointer.

The "Check" setting needs no readjustment for at least 2 hours. Air adjustment for full accuracy should be repeated every 15–20 minutes.

For oxygen deficiency testing, that is for oxygen concentrations in the range between 21 and 12%, with an accuracy of $\pm 0.5\%$ O_2 no other adjustments are needed for the life of the electrode and electrolyte (which is 2 months and up).

FIGURE 6.

For testing of O_2 in concentrations below 12%, a zero check and eventual adjustment once a week is needed. This is carried out in a very simple manner by means of a sample of nitrogen or natural gas or hydrogen, or by a special device using a miniature "sparklet" cylinder with isobutane gas, available as an accessory from the manufacturer of the instrument.

The temperature effect in the present Portable M.S.A. Oxygen Indicator has been reduced to such an extent that it is significant only in very few practical applications.

First, by using the square root scale and proper circuit characteristics the basic temperature coefficient of the detector cell has been reduced to about 0.6% per degree C. Second, our research has established the fact, that when the temperature of the unknown sample does not differ more than by $\pm 10°C$ from the temperature of the air used for standardization of the instrument, no difference within the resolution of the instrument, which is $\pm 0.1\%$ O_2, is observable. Thirdly, while no thermostat such as automatically keeps the temperature of the cell constant in the M.S.A. Continuous Model C-2 Analyzer is used, the cell is surrounded by a lucite jacket which with the substantial thermal capacity of the cell and electrolyte, and the narrow insulating air space between the jacket and the cell produces a delay of several hours in transmittance of temperature differentials to the cell. The following two experimental facts may serve as examples of the temperature characteristics of the M.S.A. Portable's detector cell: (1) Oxy-

lite, the electrolyte used in the M.S.A. detector cells, freezes at 26°–27°F. However, a Portable Oxygen Indicator has been operated for four hours at a temperature of 18° to 20°F without any sign of freezing; in other words it takes more than four hours for a cell in an instrument to get cooled down from room temperature to 27°F. (2) No deviation from the 20.8 setting was observed when air was aspirated for 15 minutes through a 5-foot sampling line from the outside where the temperature was 40°F, while the temperature inside the room was 78°F.

The span from 0 to 21% oxygen produces a change of 75 microamperes and 50 millivolts in the M.S.A. Portable Oxygen Indicator. This makes available 3.75×10^{-6} watts or 37.5 ergs/sec of power, which is about 10,000 times more than in the magnetic susceptibility type.

Tests on the M.S.A. Portable O_2 Indicator can be made while the instrument is being worn on straps. The position of the instrument is immaterial; it can even be used on its side or upside down, provided only the air adjustment is carried out in approximately the same position. This is not because of the cell characteristics, but because of the fact that the electric meter is somewhat position sensitive.

Considerable time and effort was spent in the M.S.A. Laboratory to make the instrument usable even while the user is walking. This has been accomplished only partly. It is necessary for the user to stop for 50–60 seconds after walking or after the instrument has been shaken before an Air Adjustment or a test is made. The meter pointer, when the cell is shaken, moves 5–6 divisions down or up the scale, but when standing still returns to the proper indication in less than one minute.

It is recognized that no development can be a perfect answer to any problem. As a consequence there are limitations in the use of the M.S.A. Portable Oxygen Indicator. These are: (1) The minimum drift attainable in production instruments is equivalent to approximately 0.6% oxygen per hour. For tests where the operator will be far removed from a fresh air source, as for example in certain mine rescue operations, this could be a handicap. It is recommended that in normal usage the instrument be reset on fresh air at 20 minute intervals. (2) The carbon electrode and the electrolyte require replacement with a frequency of 3 to 5 times per year whether used regularly or not. An ideal instrument would require no component replacement. (3) An oxygen free sample must be available for checking zero at weekly intervals if accurate measurements are to be made on samples containing less than 12% oxygen. (4) Where samples contain significant concentrations of strong acid gases, a scrubber should be used for their removal. Such a scrubber is available as an accessory from the manufacturer. (5) Weak acid gases such as carbon dioxide in concentrations over 25% will have an adverse effect on the instrument if sampled continuously. Where samples contain more than 25% carbon dioxide, the instrument should be briefly flushed with fresh air at intervals of aproximately 10 minutes. (6) On protracted exposure to extreme cold, the electrolyte in the cell can freeze and make the instrument inoperative. This condition, however, is immediately apparent to the operator.

The necessity of replacing electrodes and, at lower oxygen ranges, of checking zero from time to time, while listed above among the limitations, may yet prove a blessing in disguise. These operations also serve to prove to the user, that his instrument is in good working order. When using an instrument that needs no regular replacement of components, this becomes a matter of faith; and we believe, that no gas analyzing instrument is yet at the stage of perfection where such a faith would be justified.

While this oxygen indicator has several limitations, which were pointed out above, it is sincerely believed that it represents the nearest approach achieved at the present to an ideal, all around, practical portable oxygen measuring instrument for laboratory as well as for field use. Especially in the field of oxygen deficiency testing for industrial hygiene and safety purposes, where not all of the limitations apply, it will undoubtedly serve quite well for many applications.

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Nitroglycerin and Nitroglycol Exposure in an Explosives Plant

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MODERN dynamite and gelatin dynamite are composed of three basic ingredients: a sensitizer, oxidizing salts, and fillers. The common sensitizing agent is a mixture of nitroglycerin and nitroglycol, the latter compound being included primarily to increase the freezing resistance of the former. This mixture known in the trade as "oil" is the subject of the present investigation.

The toxicity of nitroglycerin is a subject that has been extensively treated in the literature through the decades. Von Oettingen[1] reviewed thoroughly the effects of nitroglycerin on the physiological functions. Laws[2] and Elbright[3] described the effects of nitroglycerin on workers engaged in its manufacture.

However, published data on the magnitude of atmospheric nitroglycerin contamination in work places in the explosives industry were found scarce and fragmentary. Elkins[4] made a single air analysis for nitroglycerin in a cordite wrapping plant. Occupational exposure to nitroglycerin was casually touched upon by Yagoda and Goldman[5] in their report on analytical procedures developed for the analysis of atmospheric contaminants containing nitrate groupings. Cook[6] briefly cited several nitroglycerin exposure values found by the United States Public Health Service as a basis upon which he first suggested in 1945 the value of 0.5 ppm as the maximum allowable concentration for nitroglycerin.

Data on the toxicology of nitroglycol are relatively meager. Gross, Bock and Hellrung[7] appear to have made a very thorough investigation concerning its toxic action on animals. Von Oettingen[1] reported that toxic symptoms in man resulting from acute exposure to nitroglycol are essentially the same as those experienced with nitroglycerin. As yet no threshold limit for nitroglycol has been proposed. Indeed there seemed to be a complete absence of any nitroglycol exposure values in the literature.

Because of this paucity of literature, and because of the persistent rumors that there might be a relationship between exposure to nitroglycerin and development of cardiac disease, the investigation discussed here was undertaken. It is pertinent to note that even as this paper was being prepared, a Swedish study of three explosives factories which also employ a sensitizer containing nitroglycerin and nitroglycol was reported in a German journal.[8] In this Swedish report medical findings as well as analyses of the atmosphere for its "nitroglycerin-nitroglycol" content carried out at different points in the factories were presented.

Raw Materials

Sensitizing oil containing 80 per cent nitroglycerin and 20 per cent nitroglycol is used in the manufacture of dynamite and gelatin dynamite or "gelly" at the plant studied. The oil component of dynamite ranges from 6 per cent to 49 per cent, of gelly from 23 per cent to 75 per cent. The raw materials employed in the making of the sensitizing oil are glycerin, ethylene glycol and a mixed acid containing equal proportions by weight of nitric and sulphuric acids.

In addition to the oil, other essential raw ingredients employed in the making of dynamite and gelly are the oxidizing salts and fillers. The oxidizing salts are ammonium nitrate and sodium nitrate. In the manufacture of gelly, nitrocellulose is an additional essential ingredient. The fillers are organic substances such as wood pulp, bagasse, corn flour, corn starch, and rice hulls. Sodium chloride, ammonium chloride and sulphur are also used. These inorganic additives are incorporated to impart specially desirable physical properties in the finished explosives. The mixture composed of the oxidizing salts, fillers, and the additives is called the "dope".

Description of Process

Various plant activities are performed in 35 buildings which are relatively small in size. The buildings are widely dispersed, obviously for reasons of safety, around the side of a hill. The nitroglycerin or "NG" factory is located on top of the hill. The plant area with the greatest potential oil exposure is the "powder line" in

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which the dynamite and gelly manufacturing operations are carried on in the following buildings: distributor house, dynamite mix house, dynamite pack house, gelly mix house, gelly stuff house, gelly hand pack house and case house.

At the NG factory, the oil is manufactured in an enclosed nitrator by adding glycerin and ethylene glycol to the mixed acid. Upon completion of the nitration reaction, the oil and the spent acid are discharged into an open separatory tank where the two materials are separated. The oil is run into an open wash tank in which it is washed with warm soda ash solution and water. The washed oil is piped by gravity down to a "Half-Way" house where it is stored, and from which the oil is fed by gravity to the distributor house as needed.

The powder line begins with the distributor house. From the storage tanks here the oil is drawn, weighed, and transported to the dynamite and gelly mix houses in covered tanks on rubber wheels or "NG" buggies. In the mix houses dynamite and gelly are produced when dopes delivered from the dope house become admixed with oil in open mixers. The explosives are removed from the mixers to uncovered wooden buggies. The loaded buggies are then transported to the pack houses where the mixes are unloaded into open hoppers or onto tables. In the dynamite machine pack house the dynamite is packed into small paper tubes or shells by machine, while large cardboard shells are packed by hand in the dynamite handpack house. Similarly, small shells of gelly are prepared and crimped by machines in the gelly stuff house and large ones hand packed in the gelly handpack house. The shells are taken to the case house, the end of the powder line. Here the shells are paraffined, boxed, and then transported to a magazine for subsequent shipping.

Sampling and Analytical Problems

Because of the inherent danger in the handling of explosive substances, investigative procedures employed had to be compatible with the safety requirements of the plant. This resulted, in many instances, in the unconventional industrial hygiene practice of sampling the working atmosphere in the powder line after the machinery was shut down and the workmen had withdrawn during the changing of shifts, either at noon or in the afternoon. The conditions investigated were considered representative inasmuch as the vaporization of the sensitizing oil would continue and the surface area of evaporation would remain essentially the same when the process equipment was temporarily shut off. The ventilation systems in the work rooms were also kept in operation.

Much thought was given to a selection of a suitable sampling method which would be practicable for the field personnel and would also collect samples considered sufficient in quantity by the laboratory. This was necessitated by plant safety requirements which forbade the use of power-driven sampling apparatus anywhere, and restricted the sampling time in most areas in the powder line to 30 minutes during the period between change in work shifts. The midget impinger apparatus was found quite satisfactory, and with this instrument all atmospheric samples were collected according to the sampling procedure for nitroglycerin used by Yagoda and Goldman.[5] The collection medium used, however, was alcohol instead of propylene glycol, since the Division's laboratory experimentally found sampling efficiency of the latter was not as high as the alcohol solution.

The analytical problems involved were much more complex than those associated with sampling. There would have been no difficulty, of course, if nitroglycerin $C_3H_5(ONO_2)_3$ alone was present as a contaminant in the plant working atmosphere since the literature related to the determination of nitroglycerin was found quite abundant. But nitroglycerin was mixed with nitroglycol $C_2H_4(ONO_2)_2$ whose volatility was reported to be 100 times greater than that of nitroglycerin.[7] In addition, oxides of nitrogen, ammonium nitrate, sodium nitrate, and cellulose nitrates or nitrocellulose had to be contended with. But it was the problem of separating nitroglycerin from nitroglycol that defied resolution.

Although methods of determination for nitroglycerin were found numerous, none was specific. There had been no specific method developed for nitroglycol, either. The Division's laboratory made quite a laborious attempt to develop a specific method for both nitroglycerin and nitroglycol. Various possible procedures investigated included polarography and infrared spectrophotometry. But the outcome was disappointing, all results being inconclusive.

In the end, a non-specific method based on colorimetric determination of nitrites as described by Rider and Mellon[8] was adopted. Necessary preliminary treatments of the samples are outlined as follows: The sample was first heated on a steambath to eliminate the inorganic nitrites. Next the organic nitrates were hydrolyzed with 15 per cent potassium hydroxide solution which reaction resulted in the release of nitrites. These preliminary treatments thus completed, the concentration of nitrites in the

form of NO_2 in the sample was then colorimetrically determined. Because the yielded nitrites could not be separated into nitroglycerin and nitroglycol, the atmospheric concentration results were expressed in three different ways in this report: (I) nitrites actually determined using the analytical method as described, (II) as nitroglycerin, and (III) as nitroglycol. It is important to note that in computing the nitroglycerin concentrations, a hydrolysis factor of 1.662 moles of nitrites per mole of nitroglycerin as was determined by Komar, Lyubimov, and Minakov[10] was applied. The hydrolysis factor for nitroglycol is unknown; so to be conservative, complete hydrolysis, i.e., two moles of nitrites per mole of nitroglycol, was assumed.

It is believed the Swedish investigators[8] might have experienced similar analytical difficulties in separating the two nitro compounds contained in the oil. They gave no description of the analytical method used, but did state that "For technical reasons the nitroglycerin and nitroglycol were determined together; the results were calculated as nitroglycerin."

Atmospheric Concentrations

A total of 42 air-borne samples were collected and analyzed according to methods described. The atmospheric concentrations found in the various buildings are shown in Table I. For purposes of general comparison it is interesting to note that nitroglycerin-nitroglycol concentrations, in terms of nitroglycerin, found in the Swedish factories[8] ranged from 0.0 mg/m³ (0.0 ppm) to 11 mg/m³ (1.18 ppm) with an over-all average less than 5 mg/m³ (0.54 ppm).

Exposure of Powder Line Workers

There were 73 production workers in the powder line and NG factory of the plant who could be grouped under twelve basic classifications. The daily exposure of the majority of these workers was essentially constant, since their activities were confined to a given building or work location. The NG factory men, powder line truckers, and NG storage men were time-studied because their duties required them to move from one area to another a number of times throughout the day. Based on the above time-study data and other observations, the weighted daily average exposure for each occupation was computed (see Table II). The general average concentration of the powder line was used as the exposure of the maintenance man who performed necessary repairs in the line only when it was completely shut down.

TABLE I

Atmospheric Concentration by Work Locations

Work location	Average concentrations, ppm		
	Nitrites (NO_2) from hydrolysis of organic nitrates	as Nitroglycerin	as Nitroglycol
NG factory	0.07	0.04	0.03
Distributor house	0.07	0.04	0.03
Dynamite mix house	0.63	0.38	0.31
Gelly mix house	0.45	0.27	0.22
Dynamite hand pack house	0.22	0.13	0.11
Dynamite machine pack house	0.43	0.26	0.22
Gelly hand pack house	0.51	0.31	0.26
Gelly stuff house	0.51	0.31	0.26
Dynamite case house	0.07	0.04	0.03
Gelly case house	0.07	0.04	0.03
Maintenance building	0.03	0.02	0.02

TABLE II

Exposure of Workers by Occupations

Occupation	Weighted average daily exposure, ppm		
	Nitrites (NO_2) from hydrolysis of organic nitrates	as Nitroglycerin	as Nitroglycol
NG factory man	0.05	0.03	0.02
NG storage man	0.10	0.06	0.05
Dynamite mix man	0.63	0.38	0.31
Gelly mix man	0.45	0.27	0.22
Dynamite hand packer	0.22	0.13	0.11
Dynamite machine packer	0.43	0.26	0.21
Gelly hand packer	0.51	0.31	0.26
Gelly stuffer	0.51	0.31	0.26
Gelly crimper	0.51	0.31	0.26
Case house man	0.07	0.04	0.03
Powder line trucker	0.12	0.07	0.06
Powder line maintenance man	0.30	0.18	0.15

Atmospheric Concentrations in Warm and Cold Seasons

In most industries, especially the dusty trades, the degree of in-plant atmospheric contamination is higher in the cold season when doors and windows are usually closed than in the warm when they are normally open. The reverse was found to be the case in this dynamite plant. Table III shows that, with few exceptions, nitroglycerin-nitroglycol concentrations in the warm season, as represented by findings gathered in August, were appreciably higher than those in the cold season, based on data obtained in January and March. The results were not unexpected, since the vapor pressures of nitro-

TABLE III

Atmospheric Concentration in Cold and Warm Seasons

Work location	Average concentration, ppm					
	Nitrites (NO_2) from hydrolysis of organic nitrates		as Nitroglycerin		as Nitroglycol	
	cold season	warm season	cold season	warm season	cold season	warm season
NG factory	0.08	0.05	0.05	0.03	0.04	0.02
Distributor house	0.02	0.08	0.01	0.05	0.01	0.04
Dynamite mix house	0.41	0.86	0.25	0.52	0.21	0.43
Gelly mix house	0.22	0.53	0.13	0.32	0.11	0.26
Dynamite hand pack house	0.12	0.33	0.07	0.20	0.06	0.17
Dynamite machine pack house	0.20	0.65	0.12	0.39	0.10	0.32
Gelly hand pack house	0.35	0.68	0.21	0.41	0.17	0.34
Gelly stuff house	—	0.51	—	0.31	—	0.26
Dynamite case house	0.05	0.08	0.03	0.05	0.02	0.04
Gelly case house	0.03	0.10	0.02	0.06	0.02	0.05
Maintenance building	0.03	0.03	0.02	0.02	0.02	0.02

glycerin and nitroglycol increased with temperature and doors in most workrooms (NG factory not included) were observed to be left open in the winter months.

The vapor pressures for nitroglycerin and nitroglycol deserve further comment. Gross, Bock, and Hellrung[7] compared the 20° Centigrade values for the two compounds reported in the literature. These investigators found the vapor pressure figures for nitroglycol agree with each other quite well, and the average value is 0.045 mm Hg. On the other hand, widely varying vapor pressures for nitroglycerin ranging from 0.00012 to 0.011 mm Hg were noted. These investigators determined the vapor pressure for nitroglycerin at 20° Centigrade as 0.00072 mm Hg, but felt 0.00038 mm Hg measured by Brandner[11] to be probably correct. Gross and his co-workers observed, in one of their many experiments involving nitroglycerin, that they could only obtain air concentrations of 0.01 mg/liter, or 1.08 ppm, at room temperature. In the light of such observations, one might question the high concentrations of 10 ppm referred to by Cook.[6]

By applying the equations derived by Brandner[11] for vapor pressures of binary solutions, the vapor pressures at 20°C of nitroglycerin and nitroglycol in a four to one mixture were theoretically found to be 0.00028 and 0.01346 mm Hg, respectively. Thus, on a vapor pressure basis the vapors volatilized from the oil handled at the plant studied would have a composition whose nitroglycol to nitroglycerin ratio is forty-eight to one. This is quite enlightening in that it shows nitroglycol is the predominant contaminant, and nitroglycerin is definitely an insignificant component of the atmospheric picture.

Ventilation Rates

The exhaust ventilation systems in the plant were checked; and where practicable, the air flow rates measured. The majority of the systems are of the general or dilution type, local exhaust of a sort being employed only in a few areas, i.e., gelly mix house, dynamite machine pack house, and the nitrator and wash tanks in the NG factory. The ventilation rates for the various buildings measured ranged from 12 to 52 air changes per hour.

Discussion

This investigation disclosed that measurable quantities of air-borne nitroglycerin and nitroglycol were present in every work location in the powder line of the explosives plant studied. However, the average values in terms of nitroglycerin reported here in no instances exceeded the presently adopted threshold limit of 0.5 ppm. These values agreed reasonably well with those obtained by the Swedish. The workman's over-all exposure should of course include a consideration of nitroglycerin and nitroglycol intake through skin absorption, tests for which were not carried out in this inhalation exposure study.

It is recognized that ideally the atmospheric samples should be chemically determined in terms of definite quantities of nitroglycerin and nitroglycol. But such an undertaking was found to be a major problem which was beyond the resources of the Division's laboratory to resolve in a reasonable period of time. Analytically, then, this should pose a challenging subject for further study. However, vapor pressure calculations have shown that sensitizing oil vapors contain principally nitroglycol, the amount of nitroglycerin present being insignificant. Practically, it would seem reasonable to regard the organic nitrates analyzed at various points of the dynamite plant as all nitroglycol.

The degree of air contamination at the dynamite and gelly mix and pack houses in the plant's powder line can be materially reduced by covering with canvas the sensitized mixes when they are not in use and the installation of effective local exhaust ventilation control

measures complete with properly designed hoods. Skin absorption of nitroglycerin and nitroglycol can be minimized by strictly observing personal cleanliness, i.e., at least one change of work clothes a day, a shower at the end of the shift, and washing of hands as often as practicable.

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Syllabus of PHS Short Courses

THE OCCUPATIONAL HEALTH PROGRAM, U.S. Public Health Service, has presented annually since 1953 two-week short courses for industrial hygiene engineers and chemists. The courses are given at the Occupational Health Field Headquarters, 1014 Broadway, Cincinnati, Ohio, usually in September. The first week of instruction is identical for engineers and chemists, and is given to the combined groups. In the second week the engineers and chemists are separated to receive instruction in more specialized areas. Primary consideration is devoted to fundamental principles and methods employed in the evaluation and control of the working environment.

A 375-page Syllabus has been developed by the teaching staff and printed for use with these courses. There are 23 lectures on sampling, analysis, measurement and evaluation of environmental factors; 10 lectures on various types of control measures; and 23 laboratory exercises for chemists and engineers. A list of selected general references sources, a special table of conversion factors, and a list of 35 engineering problem exercises with solutions are included also.

Public Health Service Publication No. 614, *The Industrial Environment . . . Its Evaluation and Control: A Syllabus for Short Courses for Industrial Hygiene Engineers and Chemists* is available from the Superintendent of Documents, U.S. Government Printing Office, Washington 25, D. C. The price is $2.75 per copy.

Relationships of an Air Quality Measurement to Meteorological Parameters*

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Introduction

A TWO-YEAR joint federal, state, and city-county air quality study was recently completed in the city of Louisville and Jefferson County, Kentucky. An extensive air sampling and meteorological network had been set up for this study. A small sample of the data collected during the course of the study was analyzed to show the relationships of an air quality measurement to meteorological parameters using graphical multiple curvilinear regressions and correlation indices.

The air quality measurement selected for use in this analysis was optical density (soiling index) which is an index of smoke concentrations. Optical density measurements are the logarithm of the ratio of the transmission of light through a clean filter to the transmission of light through a filter on which air-borne particles have collected. These data were available for continuous, consecutive two-hour sampling periods. This relatively short sampling period assisted in maintaining uniformity of the values of the meteorological parameters within the sampling period. Data representing the early morning period of the day (0000–0500 CST) were desired to minimize the effect of the diurnal trends of optical density measurements and meteorological parameters. In this analysis, the measurements for one sampling location for the period 0000 to 0200 CST during February, March, and April 1956 were used.

The meteorological parameters used in this analysis were wind speed, wind direction, temperature, and a stability index. The wind speeds, wind directions, and temperatures used were means of the two hourly average values for the sampling period. In the absence of a direct stability measurement, a stability index was calculated from surface temperature measurements. The index is the difference between the mean of the daytime maximum temperatures before and after the sampling period, and the mean temperature during the sampling period, plus the change in maximum temperatures:

$$S.I. = \tfrac{1}{2}(T_{x_1} + T_{x_2}) - T_m + (T_{x_2} - T_{x_1})$$

where S.I. is the stability index, T_{x_1} is the maximum temperature on the previous day, T_{x_2} is the maximum temperature on the day of the sample, and T_m is the mean temperature during the sampling period. Low values indicate instability and high values, stability. The meteorological measurements, made two miles from the optical density measuring site, are considered representative of the air sampling location.

Method of Analysis

The optical density data were divided into two groups, one group to be used to estimate graphically the regression curves and the other to check the representativeness of the graphical estimates for independent data from the same population. The data were divided by first ranking the optical density measurements and then by placing the odd-numbered rank values into the first group and the even-numbered values into the second group. The optical density data with missing meteorological data for the same time period were then eliminated. Forty-two cases were used to derive the relationships and thirty-four cases were used for checking purposes.

The regressions and intercorrelations (Table I) among the meteorological parameters, and the regression (Figures 1–4) and correlation (Table II) of optical density on each meteorological parameter were computed. A graphical curve-fitting method was used to estimate the regression curves. For each pair of parameters, except those which contain wind direction, the regression curves were first approximated by plotting a scatter diagram and graphically calculating and plotting moving median values of one parameter for an interval of the other parameter. Then a

* Presented at the American Industrial Hygiene Association annual meeting on April 24, 1958, Atlantic City, New Jersey.

TABLE I

Intercorrelations among Meteorological Parameters

Pairs of meteorological parameters	Correlation index	Per cent of variance explained
Wind speed on wind direction	0.42	17.6
Temperature on wind direction	0.62	38.4
Stability index on wind direction	0.52	27.0
Temperature on wind speed	0.54	29.2
Stability index on wind speed	0.65	42.3
Stability index on temperature	0.53	28.1

TABLE II

Correlations of Optical Density on Meteorological Parameters

Meteorological parameters	Correlation index	Per cent of variance explained
Wind speed	0.69	47.6
Stability index	0.49	24.0
Wind direction	0.36	13.0
Temperature	0.33	10.9

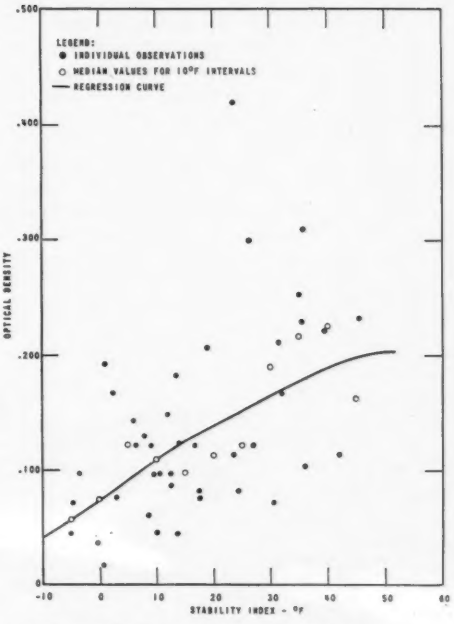

FIGURE 2. Optical density vs. stability index.

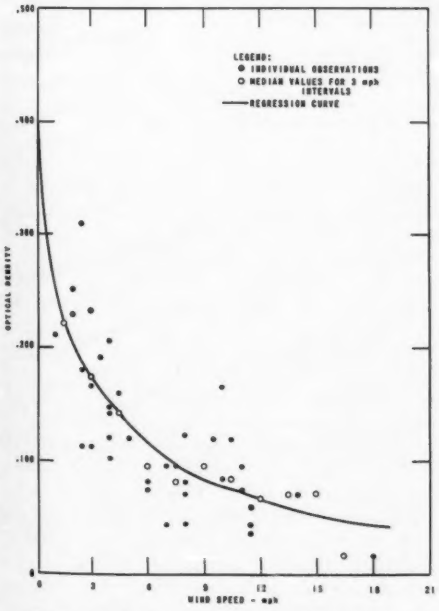

FIGURE 1. Optical density vs. wind speed.

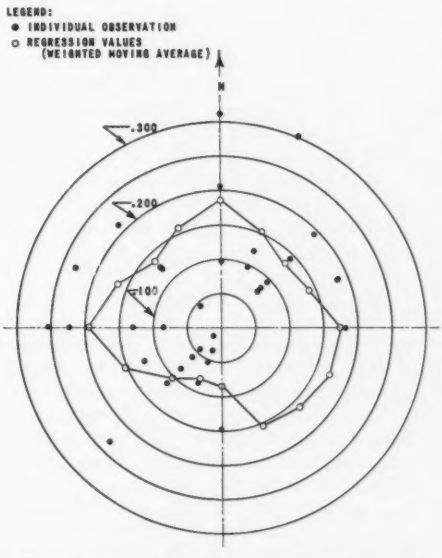

FIGURE 3. Optical density vs. wind direction.

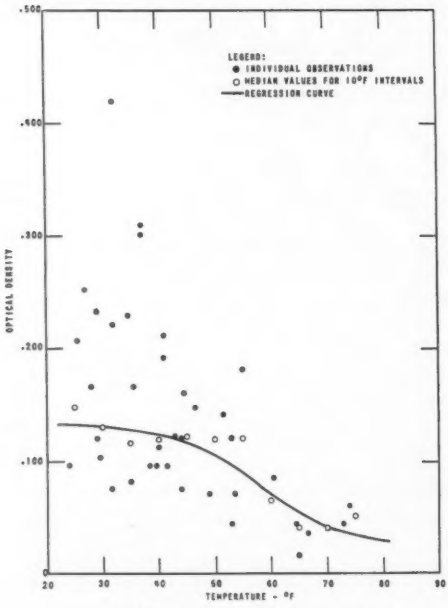

FIGURE 4. Optical density vs. temperature

smooth curve of best fit was drawn to these moving medians (Figures 1, 2, and 4). The regression values on wind direction are weighted moving average values (Figure 3), computed from the individual values for the wind direction under consideration, and the values for one compass point on either side of the direction under consideration. These averages are twice the sum of the values for the direction under consideration plus the sum of the values for the adjacent directions, divided by the sum of twice the number of observations for the direction under consideration and the number of observations for the adjacent directions. All of the correlation indices (ρ) were computed by the following formula:

$$\rho = \sqrt{1 - \frac{\Sigma(Y - Y_c)^2}{\Sigma(Y - \overline{Y})^2}}$$

where $(Y - Y_C)$ is the deviation of an individual value from its graphically estimated value as determined from the regression curve, and $(Y - \overline{Y})$ is the deviation of an individual value from the mean of all of the values. Also the percentages of the variance explained were computed by squaring each correlation index. These correlations show the total relationship of each variable to every other variable used in the study.

Two graphical multiple curvilinear regression techniques were used to show the net effect of each meteorological parameter and the total effect of all of the meteorological parameters on optical density. Both techniques considered optical density as the dependent variable and the meteorological parameters as independent variables. In each of the techniques, a regression curve was drawn for the dependent variable on the first independent variable. The relative residuals were then computed and plotted against the next independent variable. (A relative residual is the ratio of the observed value minus the regression value to the regression value.) A regression curve of the relative residuals from the first regression curve versus the second independent variable was drawn. This procedure was continued until the net effect of each independent variable was eliminated. The same procedures for the drawing of the regression curves, previously described, were used in both techniques. Cumulative correlation indices and cumulative percentages of variance explained were computed after the elimination of the effect of each independent variable so that computation could be made of the net per cent of variance explained by each independent variable after elimination of the effect of the preceding independent variables. To compute multiple correlation indices, the optical density values were estimated from the regression curves and used in one of the following formulas, depending on the number of independent variables eliminated:

$$Y_1^c = Y_1^i$$
$$Y_2^c = Y_1^i(100 + R_1^i)/100,$$
$$Y_3^c = Y_1^i(100 + R_1^i + R_2^i)/100, \text{ and}$$
$$Y_4^c = Y_1^i(100 + R_1^i + R_2^i + R_3^i)/100$$

where Y_1^c, Y_2^c, Y_3^c, and Y_4^c are calculated optical density values after elimination of the first independent variable, the first and second independent variables, the first, second, and third independent variables, and all of the independent variables, respectively; where Y_1^i is regression value from the first regression curve, and R_1^i, R_2^i, and R_3^i are relative regression values from the second, third, and fourth regression curves, respectively. After calculation of the computed optical density values, correlation indices and percentages of explained variance were computed by using the previously described formulas. The net variance explained by each independent variable after elimination of the effect of the preceding variables was then computed by subtracting the variance explained by the previous variables from the variance explained, including the variable in question. Also, standard errors of estimate (S_y) were computed for each correlation index by

using the following formula (Table IV):

$$S_y = \sqrt{\frac{\Sigma(Y - Y_c)^2}{N}}$$

The first technique presents two orders of variable elimination, one of which was selected because of its relationship to the statistical method[2] and the other because of its relationship to air quality. Only first approximation regression curves were drawn so that the order of variable elimination would be significant.

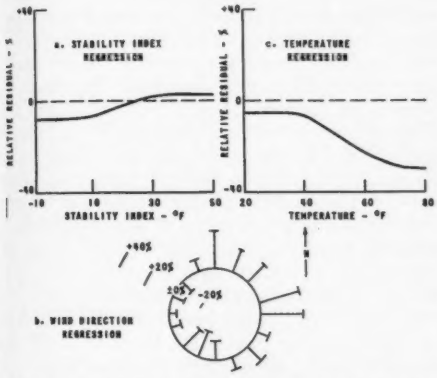

FIGURE 5. Regressions of relative optical density residuals on meteorological parameters—statistical order of elimination (see text).

TABLE III
Graphical Multiple Curvilinear Correlations

Techniques	Cumulative correlation index	Cumulative per cent of variance explained	Per cent of variance explained
A. Orders of elimination technique (1st approximations)			
1. Statistical order of elimination			
Wind speed	0.69	47.6	47.6
Stability index	0.73	53.3	5.7
Wind direction	0.79	62.4	9.1
Temperature	0.80	64.0	1.6
2. Meteorological order of elimination			
Temperature	0.33	10.9	10.9
Wind direction	0.58	33.6	22.7
Wind speed	0.67	44.9	11.3
Stability index	0.69	47.6	2.7
B. Successive approximation technique			
Wind speed	0.73	53.3	53.3
Wind direction	0.78	60.8	7.5
Temperature	0.79	62.4	1.6
Stability index	0.84	70.6	8.2

The first order eliminates the effect of each independent variable according to its total influence on optical density, as determined by the correlation indices in Table II. The order was wind speed (Figure 1), stability index, wind direction, and temperature (Figure 5 and Table III-A-1).

The second order eliminates the effect of each independent variable according to its assumed general relationship to air quality. The meteorological variables related to effective air pollution source strength are temperature and wind direction, and the variables affecting the dispersion of pollutants are wind speed and stability. Because the dispersion variables were eliminated first in the previous order of elimination, the source variables were eliminated first in this order. Therefore, the order was temperature (Figure 4), wind direction, wind speed, and stability index (Figure 6 and Table III-A-2).

The second technique used the multiple graphical curvilinear regression method, after Ezekiel.[2] This method involves a series of successive approximations which adjust the first approximation regression curves until no further adjustment can be made graphically. The method produces a net regression curve for each independent variable from which the effects of all of the other independent variables have been eliminated. Each curve is independent of order of elimination. Therefore, this method will show the net variances of optical density explained by each meteorological variable which are independent of order (Figure 7 and Table III-B).

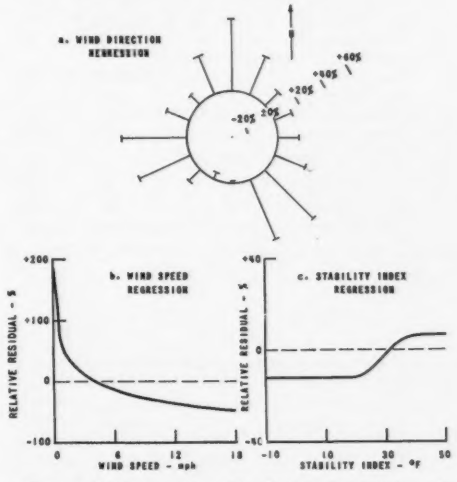

FIGURE 6. Regressions of relative optical density residuals on meteorological parameters-meteorological order of elimination (see text).

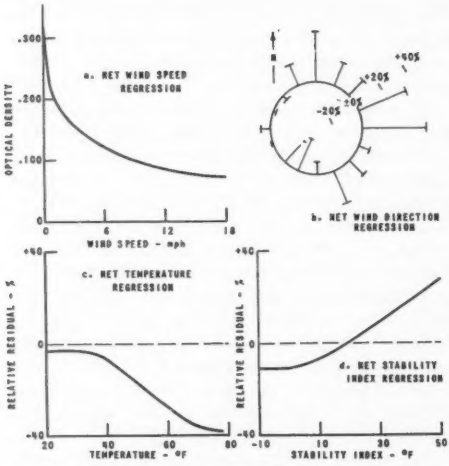

FIGURE 7. Net regressions of optical density on meteorological parameters—successive approximation technique (see text).

TABLE IV

Standard Errors of Estimate

Techniques	S_y	S'_y
A. Orders of elimination technique		
1. Statistical order of elimination		
Wind speed	±.060	±.061
Stability index	±.056	±.062
Wind direction	±.050	±.065
Temperature	±.049	±.056
2. Meteorological order of elimination		
Temperature	±.077	±.072
Wind direction	±.067	±.075
Wind speed	±.061	±.065
Stability index	±.059	±.066
B. Successive approximation technique		
Wind speed	±.056	±.063
Wind direction	±.052	±.068
Temperature	±.051	±.068
Stability index	±.044	±.068

TABLE V

Checks Using Independent Data

Techniques	Correlation Index	Per cent of variance explained
A. Orders of elimination technique		
1. Statistical Order of elimination	0.63	39.7
2. Meteorological order of elimination	0.41	16.8
B. Successive approximation technique	0.35	12.3

Checks to determine the representativeness of the regression curves for a set of independent data were made by computing the standard errors of estimate (S_y') after the elimination of each independent variable (Table IV) and the total correlation indices for each technique (Table V) of the second group of data on the sets of regression curves obtained in the two multiple regression techniques.

Results

Wind speed explains considerably more of the variance of optical density, in its total effect, than any of the other meteorological parameters (Table II), and it explains approximately one-half of the variance of optical density in its net effect after elimination of the effect of the other meteorological parameters (Table III-B). All of the regression curves relating wind speed to optical density have the same characteristics (Figures 1, 6b, and 7a). Since a check of these regression curves with independent data shows that standard errors of estimate decrease when progressing from the preceding step to the step which relates wind speed to optical density (Table IV), the form of relationship shown by the curves is valid.

Stability index ranks second in total influence on optical density (Table II). However, with the removal of wind speed effect, the amount of variance eliminated by stability is reduced considerably (Table III). Unlike the wind speed relationships, the characteristics of the stability index regression curves are not similar in all of the methods of analysis. In the total and net relationships (Figures 2 and 7d) the curves are similar, as they are also in the statistical and meteorological orders of elimination (Figures 5a and 6c). According to the check of these regression curves with the independent data, neither type of curve is representative, because the standard errors of estimate do not decrease when progressing from the preceding step to the step which relates stability index to optical density (Table IV).

Wind direction ranks third in total influence on optical density (Table II), and net effect (Table III-B). After elimination of the effect of the other meteorological parameters, the variance explained by it is reduced. Each regression curve relating wind direction to optical density is fairly consistent with the other corresponding curves showing the same relationship (Figures 3, 5b, 6a, and 7b) but, according to the independent data regression curve check (Table IV), the regression curves are not representative for the same reason that was described in the previous paragraph on the stability index parameter.

Finally, temperature ranks last in total effect

on optical density (Table II) with considerably less net influence. However, all of the regression curves relating temperature to optical density have the same characteristics (Figures 4, 5c, and 7c) and these curves are representative because of the general decrease of the standard error of estimate when the temperature regression curves are used with the independent data (Table IV).

The total correlation index is highest in the successive approximation technique and lowest in the meteorological order of elimination (Table III). According to the independent data check, the most representative method is the first technique, with the statistical order of elimination (Table V).

Discussion of the Results

It is concluded that wind speed is the most important variable in the determination of optical density at ground level. About one-half of the variance in optical density can be explained by this single parameter. A key feature of this variable is its relative independence of other meteorological variables in its relationship to optical density. The wind speed regression curves also indicate the true relationship between these two variables.

Stability index, although ranking second in total variance reduction of optical density, is very closely related to wind speed in its relation to optical density, so that most of the variance explained by stability can be explained by wind speed alone. The regression curves do not show true net or total relationships between the stability index and optical density, a deficiency indicated by the check of the regression curves with independent data.

Wind direction regression curves also are not representative. These spurious results are caused by data insufficient to produce meaningful results. A much larger sample of homogeneous data which can be classed into sixteen compass points with a significant number of cases in each wind direction is necessary to show the influence of wind direction.

This method of analysis adequately describes the relationship of temperature to optical density because the regression curves are representative. However, there is very little net temperature effect and the temperature curves may represent changes of optical density with time because of the time period of three months involved in the study. In order to separate the direct and indirect (i.e., time trend) influences of temperature several years of data for the same months would have to be analyzed.

The net effect of the dispersion variables, wind speed and stability index, on optical density is greater than the net effect of the source variables, wind direction and temperature, by a factor of approximately seven. It is concluded that the effective sources of air-borne particles measured by the optical density sampler were rather uniformly distributed about the sampling location.

It can be seen that the statistical order of elimination, using only first approximation regression curves, gives the more representative results of the two techniques presented. It is suspected that the successive approximation method tends to make too great a correction of the regression curves for individual points and not enough for general trends. The statistical order, which eliminates the effect of each independent variable according to its total influence on the dependent (air quality) variable, would, in general, be expected to yield the better results.

Evaluation of the Study

This study represents only a small portion of the data restricted to one sampling location, one time of day, one season of the year, and one type of air sampling data. It is believed that valid relationships of wind speed and temperature to these optical density data were found using this method, but the stability index and wind direction relationships are questionable.

This method of analysis, however, does provide a useful first approximation to a refined objective method of detemining the amount and character of the relationships of an air quality measurement to measureable meteorological parameters.

Acknowledgments

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A Solenoid-Operated Microburet for Producing Uniform Droplets*

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Introduction

IN toxocological studies it is sometimes necessary to apply small doses in the form of droplets to small surfaces, for example, a guinea-pig's eye. This report describes a microburet which produces single uniform droplets, the release of which is controlled by the operator. The volume of the smallest droplet delivered is approximately 2×10^{-6} ml and the largest is 45×10^{-6} ml. This device may be made in the laboratory cheaply, since the most costly part is a solenoid valve.

Drops smaller than 2.0 mm in diameter are difficult to produce even from a fine hypodermic needle, since a drop must be heavy enough to overcome the force of surface tension in order to fall off. Lane[1] devised a microburet which overcame this difficulty by means of an axial annular jet of air surrounding the needle, which detached a series of drops of 300 microns from the tip before they had reached full size. Modifications were made by Levvy[2] and Ainsworth[3] so that single droplets were obtained only when released by the operator. This report describes a simpler modification in which the release of single droplets is obtained by the action of a solenoid valve.

Description

Figure 1 is a schematic drawing of the solenoid operated microburet. A fine 1½-inch #26 hypodermic needle (A) was attached in a vertical position to one arm of a bent capillary tube (B), and was inserted into a hollow machined brass block (C) through which was drilled a 1/32-inch bore. The slip joint of the needle was seated tightly into the aperture of the bore at the top of the block and the point of the needle protruded ½ inch through the bottom. The block, essentially the same as Lane's, provided for an airflow which escaped from the hole at the bottom to form the annular stream around the extrusion of the needle. The outside dimensions of the block were 1 x 1 x 1½ inches; the hollow chamber inside was a bored cylindrical hole large enough to fit a standard ⅛-inch pipe threaded for a standard ⅛-inch connector. The outer diameter of the needle was 0.127 inch which gave an annular space around the needle of 0.00927 inch. It was found that the liquid spread over the lower surface of the block if the needle protruded less than ⅛ inch.

The glass capillary tube, four inches long with two right angle arms, had a bore of approximately 0.5 mm. The shorter arm was connected to the slip joint of the needle and the longer one dipped into a glass reservoir (D). The dimensions of the reservoir and the two arms were such that the level of the liquid in the reservoir was lower than the level at the point of the needle in order to prevent siphoning. Two or 3 ml of liquid was used in a reservoir of 6 ml capacity. The space above the liquid was connected to a regulated source of air to provide static air pressure which caused a flow of liquid through the capillary needle. A metering valve and adjustable leak were provided to control closely the static pressure in the reservoir.

To obtain repeatable results it was found essential to use a solenoid valve (E) which was quick-acting at low pressures (0–10 psi) and which cut off the air blast sharply. A model which met these requirements was a single spring-return valve with a ¼-inch outlet. When the inlet pressure was 5 psi, the flow from the outlet was 1 cfm. The electric circuit of the solenoid was closed and opened by the follower of the cam in a conventional commercially obtainable cycling timer (F), which is a unit consisting of a microswitch, a split-face cam and an induction motor. The cam was rotated by a one-watt 15 rpm motor which was started and stopped by a switch (G). The width of the groove of the split cam and its rate of rotation determined the duration of the air pulse. Once the width of the groove was adjusted, the time pattern of the action of the solenoid valve was repeatable and consequently each air pulse was nearly identical. To obtain a single drop, switch (G) was closed and then opened after the release of the drop. To obtain a series of drops, the switch was kept closed until the required number of drops had been released. Since only a small

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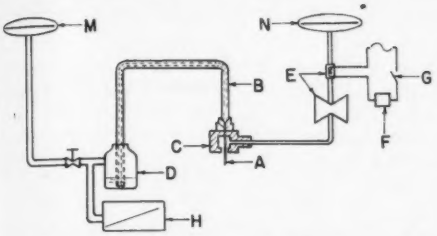

FIGURE 1. Solenoid Operated Microburet. Legend: A. hypodermic needle; B. capillary tube; C. air-pulse block; D. liquid reservoir; E. solenoid valve, model #15B-22-81, manufactured by Valvair Corp., Akron, Ohio; F. cycling timer; H. inclined tube oil manometer.

static air pressure was needed to keep the liquid flowing in the glass capillary tube and to form drops, an oil manometer (H) inclined at 30° was used to measure reservoir pressures. An electric counter was inserted to count the number of drops.

Performance Evaluation

The performance of the device was tested with respect to its reliability in releasing uniform drops and its stability in reproducing the same drop volumes. Three different settings were made of the reservoir and the solenoid pressures, to produce drops of three sizes, approximately 450, 250, and 150 microns in diameter. (One micron equals 10^{-3} mm.) For each setting of pressures, several series of drops were released to determine drop volumes. Each setting of pressures was made on three different days to determine whether the drop volumes were reproducible.

A filtered solution of dibutyl phthalate containing eight per cent betanaphthol, as a tracer, was used as the liquid for drops, primarily because of its low vapor pressure and its low viscosity. At the prevailing room temperatures, its density was approximately 1.02 gm/cm^3; its kinematic viscosity was 13 centistokes; its surface tension was 33 dynes/cm. The volume of dibutyl phthalate collected as drops was determined by the color developed by the action of diazo-sulfonic

TABLE I

Performance of the Solenoid Microburet Adjusted to Produce Large Drops

Date	Ambient conditions		Pressures (above atm.)		Number of drops on each plate	Volume of drops on each plate	Volume per drop	Calculated average drop diameter
	Barometric pressure	Temperature	Reservoir manometer	Solenoid gauge				
	cm Hg	°C	mm H_2O	lb/in.^{2}		ml × 10^{-6}	ml × 10^{-6}	microns
Feb. 28	76.6	23.8	75.0	1.67	27	1208	44.7	436
					15	665	44.3	
					32	1395	43.6	
					41	1857	45.3	
					19	852	44.8	
					25	1071	42.8	
					35	1508	43.1	
							av. 44.1 ± 2.1%	
Mar. 1	75.7	23.3	76.5	1.67	34	1576	46.4	444
					21	949	45.2	
					37	1724	46.6	
					15	685	45.7	
					33	1518	46.0	
					17	767	45.1	
					28	1287	46.0	
							av. 45.9 ± 1.2%	
Mar. 8	76.2	23.8	75.5	1.67	29	1280	44.1	440
					31	1412	45.6	
					27	1189	44.0	
					26	1139	43.8	
					39	1757	45.1	
							av. 44.5 ± 1.6%	

Average of volumes obtained on the days: 44.8 × 10^{-6} ml. ± 2.1%

TABLE II

Performance of the Solenoid Microburet Adjusted to Produce Drops of an Intermediate Size

Date	Ambient conditions		Pressures (above atm.)		Number of drops on each plate	Volume of drops on each plate	Volume per drop	Calculated average drop diameter
	Barometric pressure	Temperature	Reservoir manometer	Solenoid gauge				
	cm Hg	°C	mm H_2O	lb/in.^{2}		ml × 10^{-6}	ml × 10^{-6}	microns
Feb. 18	76.6	24.5	51.0	3.75	77	647	8.40	250
					99	847	8.56	
					70	581	8.30	
					78	676	8.67	
					77	676	8.78	
					59	495	8.40	
							av. 8.52 ± 1.8%	
Feb. 20	76.6	23.7	52.0	3.75	101	882	8.73	250
					103	902	8.82	
					60	512	8.53	
					70	600	8.57	
					103	882	8.56	
					114	997	8.75	
							av. 8.69 ± 1.4%	
Feb. 26	75.7	23.8	51.5	3.75	101	917	9.08	258
					103	926	8.99	
					102	900	8.82	
					58	512	8.83	
					114	1023	8.97	
					88	794	9.02	
							av. 8.95 ± 1.2%	

Average of volumes obtained on the 3 days: 8.68 × 10^{-6} ml. ± 2.4%

TABLE III

Performance of the Solenoid Microburet Adjusted to Produce Small Drops

Date	Ambient conditions		Pressures (above atm.)		Number of drops on each plate	Volume of drops on each plate	Volume per drop	Calculated average drop diameter
	Barometric pressure	Temperature	Reservoir manometer	Solenoid gauge				
	cm Hg	°C	mm H_2O	lb/in.^{2}		ml × 10^{-6}	ml × 10^{-6}	microns
Apr. 19	77.2	26.5	27.0	7.67	108	200	2.04	156
					119	242	2.03	
					113	217	1.92	
					112	220	1.96	
					182	89	2.04	
							av. 2.00 ± 2.5%	
Apr. 29	76.6	26.5	25.5	7.75	101	204	2.02	156
					113	230	2.03	
					93	181	1.95	
					207	410	1.98	
					101	194	1.96	
					103	210	2.03	
							av. 2.00 ± 1.5%	
Apr. 30	76.6	26.7	25.0	7.75	128	249	1.95	156
					123	256	2.00	
					143	285	1.99	
					83	160	1.92	
							av. 1.98 ± 1.5%	

Average of volumes obtained in the 3 days: 2.00 × 10^{-6} ml. ± 1.6%

acid on the betanaphthol tracer in an alkaline solution. To establish the sensitivity and the reliability of the method, ten samples were made of 0.006% solutions of the drop liquid in ethanol. It was found that one scale reading of the colorimeter represented 8.2×10^{-6} ml dibutyl phthalate with the tracer, and the standard deviation of the average of the readings of the ten samples was 2.7%

The determination of the volume of a single drop was made as follows. A series of drops was released from the microburet and caught on a clean glass plate placed four inches below the needle. A count of each drop was kept by an electric counter. After 15 to 215 drops had been collected, the liquid was washed off the slide with 10 ml ethanol. The total volume was determined by the colorimetric method. The volume of each drop was calculated by dividing the total volume by the number of drops. Photomicrographs were made of several series of drops collected on plates.

Representative data and results are shown in Tables I, II, and II. The average volumes of the drops, which were released for the testing of the microburet, were: 44.8×10^{-6} ml $\pm 2.1\%$, the largest; 8.66×10^{-6} ml $\pm 2.4\%$, an arbitrarily chosen intermediate size; and 2.00×10^{-6} ml $\pm 1.6\%$, the smallest which was reproduced reliably. Under controlled conditions in a single run, the volumes of the single drops were uniform within the experimental error of the colorimetric method; since the per cent standard deviations of the average drop volumes fell between 1.2% and 2.5%, whereas that of the colorimetric standard solutions was 2.7%. Figure 2 is a photomicrograph of a randomly chosen series of drops which represent the typical appearance of a series. If the experimental conditions were approximately the same on different days, the microburet released drops of the same volume within the experimental error of 2.7%, since the per cent standard deviations of the means fell between 1.6% and 2.4%.

Operation

For satisfactory operation, the liquid in the microburet should be free of dirt and air bubbles,

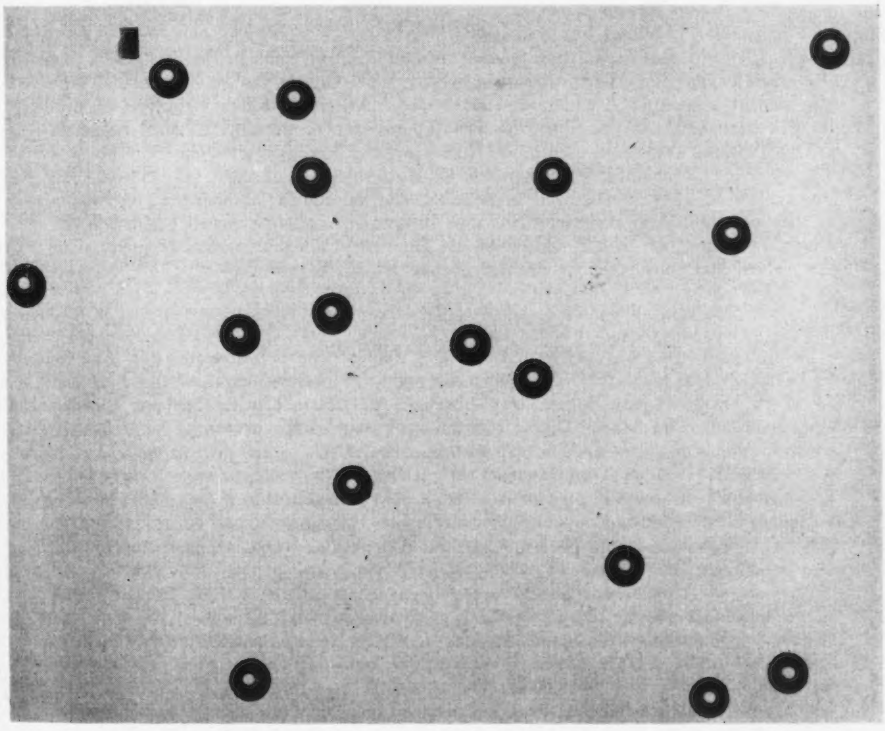

FIGURE 2. Drops of dibutyl phthalate released by solenoid-operated microburet. (Magnification 20 ×)

and the entire apparatus should be mechanically stable and free of leaks. A preliminary check may be made by permitting several large drops to form and to fall off the needle by their own weight. If they are the same size and fall at regular intervals, the device may be considered free of clogs or leaks. In using the microburet for the first time the following operating principle should be kept in mind: to decrease the drop size, it is necessary to decrease the pressure in the reservoir and also to increase the pressure on the solenoid; to increase the drop size on the other hand, it is necessary to increase the reservoir pressure and decrease the solenoid pressure. To start, it might be well to apply an arbitrary small air pressure to the reservoir, for example, 50.0 mm H_2O above atmospheric; and to let the air pulse flow for an arbitrary time duration, for example, 0.5 second, by fixing the width of the groove in the split face cam or the rpm of the motor. The pressure on the solenoid then may be adjusted by trial and error so that only one drop is produced each time the microswitch actuating the solenoid is closed.

Acknowledgment

The author is grateful to several members of the Directorate of Medical Research, U. S. Army Chemical Warfare Laboratories: to Dr. P. B. McNamara for suggesting the problem; to Mr. G. Stanley Woodson for computations.

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Obituary

DR. PAUL S. RICHARDS, a pioneer in industrial medicine in the western states, died in Salt Lake City on November 20, 1958. Only a few days before this he presided at a meeting at which final plans were made for the newly established and incorporated Richards Memorial Medical Foundation to promote medical research.

Dr. Richards graduated cum laude from Harvard Medical School in 1919. He was a member of the committee whose work led to the passage of the Utah occupational disease law in 1941. Recognized as an authority on industrial medicine, he was a charter member of the American Board of Industrial Medicine, member of the AMA Council on Industrial Health, fellow of the American College of Surgeons, member of the AIHA, and consultant to the U.S. Public Health Service.

Atmospheric Analysis Courses

TWO COURSES OF TRAINING in air pollution analyses will be offered by the U. S. Public Health Service at Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio, in March. These are one-week courses for personnel from health, control, educational, research, and industrial groups. There are no tuition fees.

Physical Analysis of Atmospheric Particulates will be given March 16–20, 1959. The physical behavior and properties of small solids dispersed in the atmosphere, the various sampling methods, evaluation criteria, size distribution, and concentration of pollutants will be included in discussion and instruction. Biological particulates will also be considered.

Analysis of Atmospheric Inorganics will be given March 23–27, 1959. In this course emphasis will be placed on the qualitative and quantitative analyses of inorganic particulates with a significant portion of time devoted to laboratory practice. Special attention will be given to the applicability and limitations of existing methods.

For additional information or applications for enrollment, write to Chief, Air Pollution Training, Robert A. Taft Sanitary Engineering Center, 4676 Columbia Parkway, Cincinnati 26, Ohio.

A Technique for the Radioautography of Alpha-Active Aerosol Particles on Millipore Filters

J. T. QUAN

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Introduction

ALPHA-RADIOACTIVE aerosol particles resulting from nuclear experiments constitute a potential inhalation and ingestion hazard. A common method of determining the extent of this hazard is by air filtration using millipore filters which have high collecting efficiency and good surface retention properties. Total radioactivity assay[1] does not present difficulties, but a satisfactory method to locate and identify individual alpha-active particles is not available. Contact radioautography[2, 3] which requires separation of particles and nuclear emulsion for photographic processing makes subsequent realignment of active particles and film spots tedious and uncertain. Any analytical method which necessitates the removal of radioactive material from the millipore filter involves risk of some loss of material.

A good approach to solving the problem of correlating a radioactive particle with its film spot was made by LaRiviere and Ichiki.[4] They permanently bonded beta-active aerosol particles collected on a thin glass surface to the inert backing of a nuclear emulsion. The physical separation provided by this backing caused the particle and its corresponding spot to appear in different focal planes when observed under an optical microscope at high power.

In the present investigation, this principle is used in conjunction with a new sample preparation technique which permanently bonds aerosol particles between a nuclear emulsion and a millipore filter. Radioautographs are made of alpha-emitting particles *in situ* on millipore filter. After the filter is transparentized, identification of these particles is easily made, and their sizes and shapes may be determined.

Equipment List

Stainless steel (ss) frame, 0.025 inch thick and 1½ inches square with centered ⅝-inch hole.

Collodion stock solution: USP flexible collodion diluted one part to three parts amylacetate.

Double hoop membrane-suport of wire (Figure 1a).

Acetone.

Liquid gelatin binder[4]—to a warm solution of one gm gelatin dissolved in 35 ml water, add a solution of 100 mg chrome alum dissolved in 15 ml water and two ml glycerin.

Kodak Autoradiographic Permeable Base Safety Stripping Film-Experimental (emulsion sensitivity approximates Kodak NTA and NTB), Eastman Kodak Co., Rochester, N. Y.

Desiccator and light-tight boxes.

Procedure

The millipore filter (MF) with the contaminated surface upward is cemented over the hole in the ss frame (Figure 2) using collodion as adhesive, and allowed to dry.

A collodion membrane is formed by placing 4–6 drops of the collodion solution on the surface of distilled water and allowing the solvent to evaporate. A double hoop support is used to lift the membrane from the water surface. The inner hoop is made large enough to allow the ss frame to pass through, while the outer one prevents folding over of the excess collodion on the inner one.

The frame is placed on top of a small block about one inch high and the hoop containing the collodion is centered over the frame and brought down past it. Better adherence of the membrane to the frame may be secured by breathing immediately on them. Under normal circumstances direct adhesion of the collodion to the MF will not take place.

A small beaker partially filled with acetone is brought just to boiling over a hot plate and removed. When vapor bubbles are no longer given off the frame is placed on the beaker so that the warm vapors pass through the hole, then through the MF, and finally to the collodion membrane. The MF is severely contorted

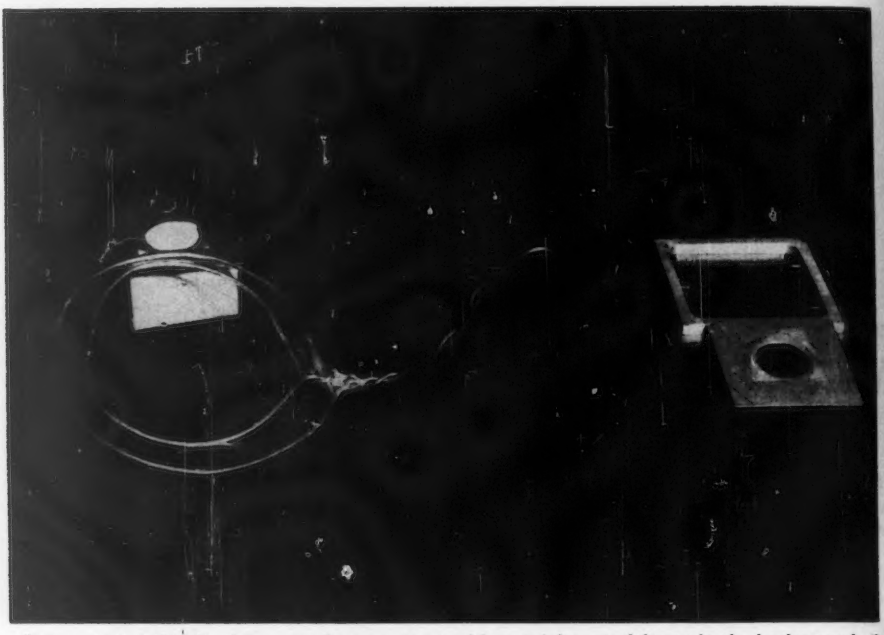

FIGURE 1. (a) Double hoop membrane-support with a stainless steel frame in the background. (b) A frame and the frame carrier used to facilitate movement on a microscope stage.

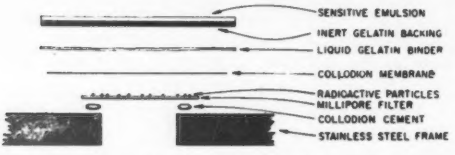

FIGURE 2. Relative positions of the components mounted for radioautography (not drawn to scale).

at first, but it soon flattens out and stretches tightly across the hole with the membrane adhering firmly to it. This process is complete in approximately two minutes. When properly done a drop of water placed on the collodion side of the preparation should show no penetration to the MF.

To protect the MF against contamination in subsequent operations, the hole is sealed with a microscope cover glass using either stop cock grease or liquid balsam as a temporary bonding agent. Then an added seal of collodion solution is applied at the edges of the cover glass.

In a photographic darkroom, the preparation with the collodion-covered particles facing upward is submerged in a petri dish of liquid gelatin bonding medium. No wetting of the MF should occur, or subsequent clearing would be impaired. A square of Kodak Autoradiographic Permeable Base Film-Experimental is floated on the surface of the gelatin with sensitive emulsion upward. The ensemble is lifted out of the gelatin with the film lapping over the leading edge by ⅛ inch to minimize the tendency of the film to slide about. It is allowed to drain, and then any excess liquid is wiped off.

Drying is done in a desiccator. Samples requiring radioautographic exposures in excess of 1–2 hours are transferred to a light-tight box after that time to prevent over-drying of the film, which can result in peeling.

Rapid photographic processing minimizes any possibility of movement between film and sample surface. The film is developed 1½ minutes in D-19, rinsed in water for a few seconds, fixed for two minutes, washed for five minutes, and dried.

The cover slip sealer over the hole is lifted off with a razor blade, and the temporary bonding material removed. The ensemble is placed on a flat surface, and 0.5 ml of the collodion solution is gently flowed onto the MF and allowed to dry.

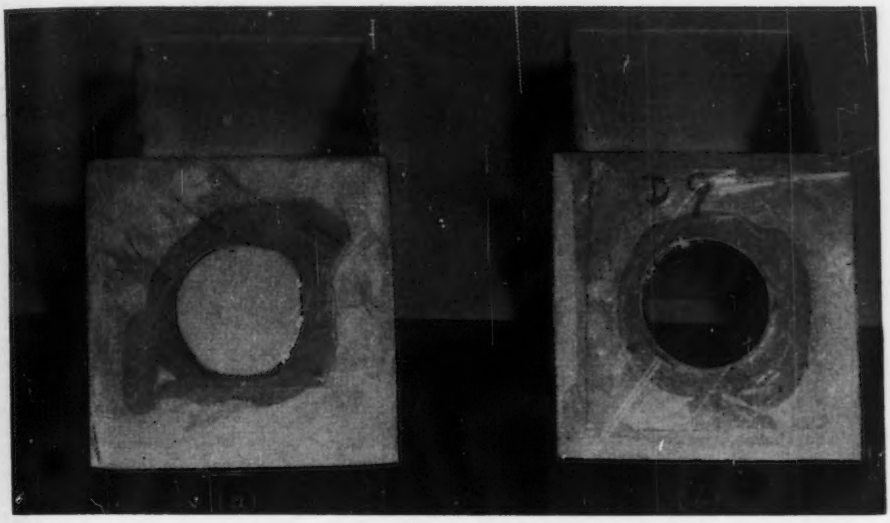

FIGURE 3. (a) Radioautographic assembly with opaque millipore filter before clearing. (b) An assembly after complete clearing. The splatter effect is caused by surface light reflection from localized irregularities.

The resulting preparation consists of radioactive particles firmly and permanently bonded between two transparent surfaces. One surface is the processed photographic film, and the other is a millipore filter rendered transparent and resilient by collodion (Figure 3).

Discussion

Collodion serves equally well in all its functions—as as cement, as a membrane, as a sealer, and as a millipore filter clearing agent.

The uniformly thin collodion membrane has low absorption for alpha radiation, and it serves three purposes. It secures the aerosol particles to the filter surface, prevents the solution of water-soluble filtered material, and it protects the filter against wetting by the liquid gelatin binder.

In order to secure the particles, good adhesion between the collodion membrane and millipore filter must be promoted. Liquid acetone dissolves both materials readily, but when only warm acetone vapor is passed through the porous millipore filter to the membrane, it condenses on the membrane in amounts sufficient to cause auto-adhesion of membrane and filter without rupturing either. Satisfactory execution of this step of the procedure is most essential to the success of the entire technique.

The Kodak autoradiographic permeable base film is especially suited to this experimental technique because its sensitive emulsion is backed by a five micron layer of plain gelatin. This backing does not attenuate alpha radiation excessively, and it provides the uniform and necessarily close separation between emulsion and radioactive source. The floating of the film on the liquid gelatin surface prior to placing it in contact with a mounted aerosol sample relieves any residual strains on the film. Furthermore, it minimizes the unevenness which occurs if a thin dry film were applied directly to a wet surface.

The use of ordinary immersion fluids with a refractive index of 1.51 to clear millipore filters presents such problems as questionable stability of the preparation over extended periods, and, more important, possible movement of the aerosol particles away from their original sites. Fortunately, collodion possesses the properties required to make a sample preparation transparent, dry and permanent.

To facilitate traversing of the specimen on the microscope stage and to minimize the possibility of scratching the emulsion, a carrier such as the one shown in Figure 1b is used to hold the frame. Supported with the hole facing upward, the radioactive particles are located directly above their respective tracts.

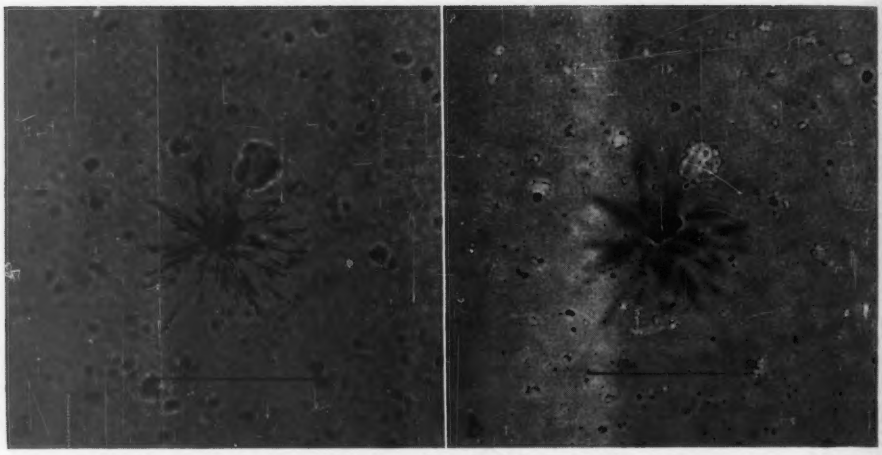

FIGURE 4. Two-hour exposure—Kodak Permeable Base Film. (a) Photomicrograph of alpha tracks from a defocussed aerosol particle. (b) The size and shape of the aerosol particle are easily discernible.

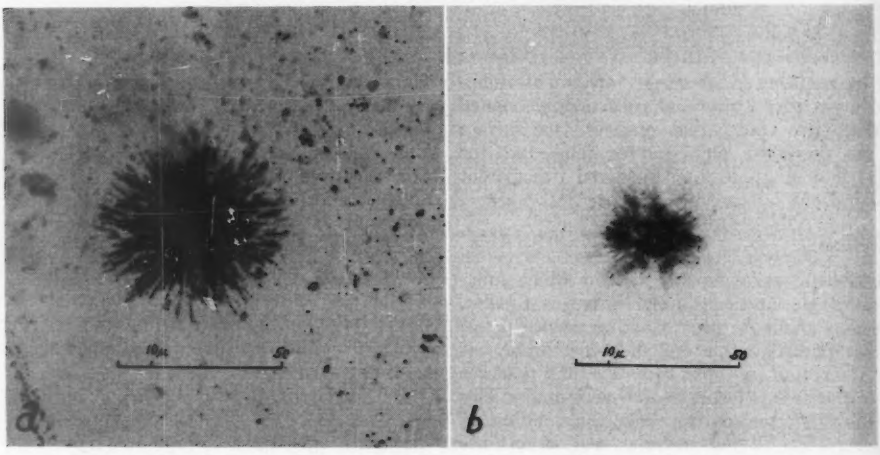

FIGURE 5. Two-hour exposure—Kodak Permeable Base Film. (a) Fairly dense spot of alpha tracks completely obscuring its source. (b) The alpha-active aerosol particle against a defocussed background of its tracks.

Results

The accompanying photomicrographs illustrate results obtained with this technique. Figure 4a shows the alpha tracks in sharp focus. The particle from which the tracks originated is in sharp focus in Figure 4b; many more non-radioactive ones are present in the same focal plane. The bright rim about the particle may be due to light interference from entrapped air and gelatin binder. The size and irregular shape of this alpha-emitter are easily discernible.

Figure 5a shows a denser spot of tracks which obscures the source. Direct particle-to-emulsion techniques would not resolve these two components. Figure 5b shows size and shape quite well.

An extremely heavy concentration of alpha tracks is shown in Figure 6a. The overall dimensions and shape suggest a single large par-

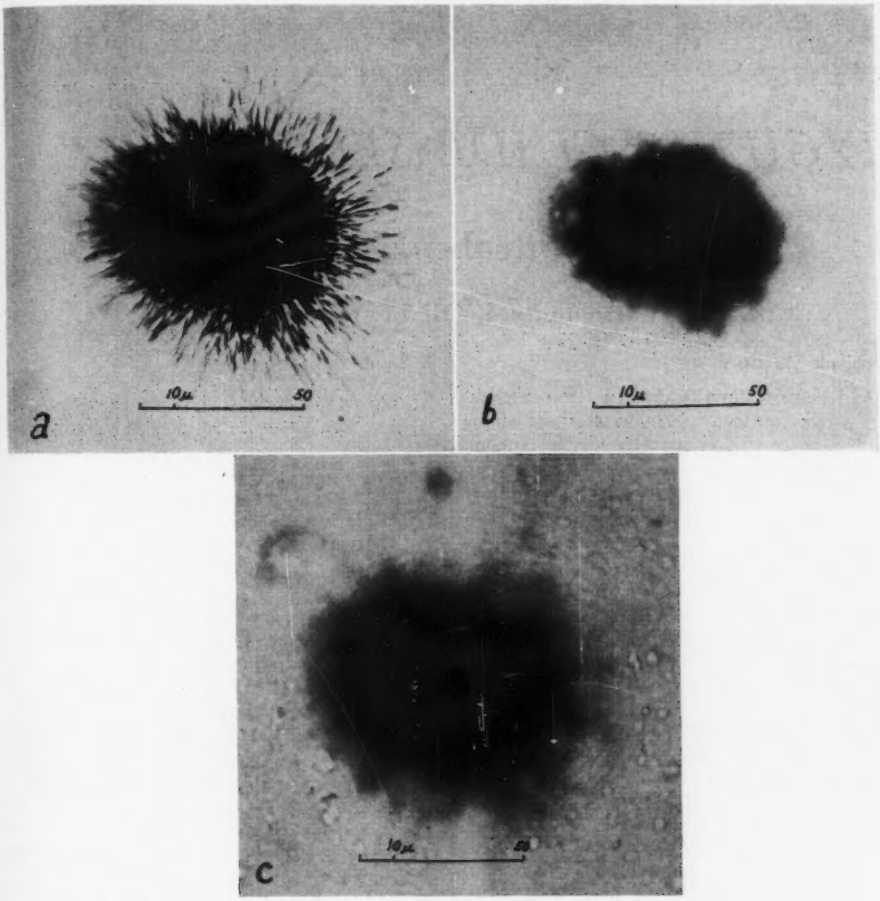

FIGURE 6. Two-hour exposure—Kodak Permeable Base Film. (a) An extremely heavy concentration of alpha tracks. (b) The spherical aerosol particle from which the tracks originated. (c) Addition of vertical illumination brings out some surface details.

ticle as the source. Figure 6b shows the shape of the radioactive particle. Its varying light transmission properties indicate inhomogenous density. With the aid of vertical illumination in Figure 6c, surface irregularities are detectable.

Acknowledgments

The author is indebted to W. B. Lane for providing the aerosol samples and to J. D. O'Connor for his aid in the laboratory.

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HYGIENIC GUIDE SERIES

Nitrobenzene

(Nitrobenzol, Oil of Mirbane)

I. Hygienic Standards

A. RECOMMENDED MAXIMUM ATMOSPHERIC CONCENTRATION (8 hours): 1 part of vapor per million parts of air, by volume (ppm).[1]

(1) *Basis for recommendation:* Animal experimentation,[2, 3] and human experience.[4, 7]

B. SEVERITY OF HAZARDS:

(1) *Health:* High, for both acute and chronic exposures. Absorption by any route, including the skin, may lead to severe toxicity or death. Nitrobenzene may affect: (a) the nervous system, giving rise to fatigue, vertigo, headache, vomiting, and general weakness, and signs of central nervous system involvement, such as altered pulse and respiration and skin temperature changes; (b) the blood, producing methemoglobinemia and lowered red cell count; (c) the spleen and liver, with jaundice a possibility. Subacute and chronic responses may follow repeated exposure, with anemia the salient sign. Nervous symptoms may also be present.

(2) *Fire hazard:* Moderate, when exposed to heat or flame. Flash point: 190°F (closed cup).

C. SHORT EXPOSURE TOLERANCE: 200 ppm may be inhaled for one hour without serious disturbance; slight symptoms may appear after a few hours exposure to 40–80 ppm.[3]

D. ATMOSPHERIC CONCENTRATION IMMEDIATELY HAZARDOUS TO LIFE: May be almost immediately fatal if significant areas of body are in contact with liquid or clothing saturated with liquid. Inhalation of massive concentrations may likewise prove rapidly fatal.

II. Significant Properties

Almost water-white, oily liquid, turning yellow with exposure to air. Odor like that of bitter almonds which persists at high dilution.

Chemical formula:	$C_6H_5NO_2$
Molecular weight:	123
Melting point:	5.7°C
Boiling point:	210.9°C
Specific gravity:	1.199 (25°/4°C)
Relative vapor density:	4.25 (air = 1)
At 25°C and 760 mm Hg,	
1 ppm of vapor:	0.00503 mg/liter
1 mg/liter vapor:	198.8 ppm
Solubility:	Immiscible in water; miscible with alcohol and ether; excellent solvent for many organic compounds.

III. Industrial Hygiene Practice

A. RECOGNITION: By its almond-like odor. Major uses: manufacture of aniline dyes and explosives and as intermediate and solvent for other industrial organic substances.

B. EVALUATION OF EXPOSURE: The following methods will evaluate atmospheric exposures only—not skin absorption:

(1) *Direct instrumentation:* None. Polarographic methods have been shown to be applicable.[6]

(2) *Chemical method:* Absorption in nitrating acid and determined as dinitrobenzene.[5]

C. Recommended control procedures: Manufacturing processes should be enclosed where possible and adequate ventilation provided to reduce air concentration below 1 ppm. Compressed air or aspiration should be used to fill or empty receptacles. Floors should be impermeable and not composed of asphalt, tar or other substance capable of retaining nitrobenzene. Opportunities for skin absorption either directly or through clothing should be eliminated. Suitable protective clothing should be provided to prevent contact. Workmen should be instructed in proper procedure in event of spill or body contact with nitrobenzene.

IV. Specific Procedures

A. First aid: If spills occur on body, immediately place the individual in a shower and remove clothing. Assistance should be given in the event of collapse. Clean hair and nails thoroughly with soap and water. Call physician immediately. Treatment should be for central nervous system collapse and shock, keeping patient warm and at rest. Methemoglobin determination is best measure of progress of patient.[7]

B. Specific medical procedures:

(1) *Preplacement:* Individuals suffering from anemia, cardiovascular or pulmonary disabilities should not be employed for work with nitrobenzene.

(2) *Periodic:* Medical inspection of personnel is desirable. Medical assistance should be within immediate call at all times. Examination of the urine may be helpful in the periodic inspection. Dark-colored urine, arising from p-aminophenol, the chief metabolite of the nitrobenzene, is an indication of over-exposure.

V. References

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Meta-Dinitrobenzene

(DNB)

I. Hygienic Standards

A. Recommended maximum atmospheric concentration (8 hours): 1 milligram per cubic meter of air (mg/m^3).[1]

(1) *Basis for recommendation:* Animal experimentation,[4, 6] and human experience.[2, 6]

B. Severity of hazards:

(1) *Health:* High, for both acute and chronic exposures, although chronic effects are more commonly encountered. Skin absorption is the more important source of injury. Inhalation of dust may occasionally result in poisoning. Vapor inhalation may also constitute an exposure source as DNB is volatile with steam. Chief action of DNB is production of methemoglobin and reduction in red-cell count. Acute poisoning shows signs of central nervous system involvement with depression, numbness, staggering gait, somnolence, and loss of consciousness. Cyanosis and vertigo may persist for weeks. Subacute and chronic poisoning presents similar signs and often increased sensitivity with increased exposure. Cyanosis is a prominent feature. Acute exacerbation may occur on exposure to heat, sun, or alcoholic intake. Acute necrosis of liver may occur.[2] Industrial fatalaties from DNB are now rare.

(2) *Fire:* Slight, when exposed to heat

or flame. Flash point is 302°F (closed cup).

(3) *Explosion hazard:* Severe, when exposed to shock or flame. High explosive if mixed with oxygen carriers. Emits toxic fumes.

C. SHORT EXPOSURE TOLERANCE: Unknown.

D. ATMOSPHERIC CONCENTRATION IMMEDIATELY HAZARDOUS TO LIFE: Unknown.

II. Significant Properties

The meta derivative is a solid at ordinary temperatures; colorless and odorless when pure. Industrial product may be faintly yellow.

Chemical formula:	$C_6H_4(NO_2)_2$
Molecular weight:	168.1
Melting point:	90° C
Boiling point:	303° C
Specific gravity:	1.571 at 0°/4° C
At 25° C and 760 mm Hg,	
1 ppm vapor:	0.00687 mg/liter
1 mg/liter of vapor:	145.5 ppm
Solubility:	Slightly soluble in cold, more soluble in hot water; soluble in alcohol, and in a number of other organic solvents.

III. Industrial Hygiene Practice

A. RECOGNITION: No marked physical characteristics for identification. Used extensively in manufacture of dyes and explosives.

B. EVALUATION OF EXPOSURE: The following methods will evaluate atmospheric exposures only—not skin absorption:

(1) *Direct instrumentation:* None available. Polarographic methods have been shown to be applicable.[5]

(2) *Chemical method:* Collect in alkali and measure color directly.[3] Air analysis is of value in control of exposures only if skin absorption is prevented.

C. RECOMMENDED CONTROL PROCEDURES: Manufacturing processes should be enclosed where possible and adequate ventilation provided to reduce exposures below 1 mg/m³. Opportunities for skin absorption, either directly or through clothing, should be eliminated. Suitable protective clothing should be provided to prevent contact. Workmen should be instructed in proper procedure in event of spill or body contact with dinitrobenzene.

IV. Specific Procedures

A. FIRST AID: If contact with DNB occurs on body, immediately place the individual in a shower and remove clothing. Assistance should be given in the event of collapse. Clean hair and nails thoroughly with soap and water. Call physician immediately. Treatment should be for central nervous system collapse and shock, keeping patient warm and at rest. Methemoglobin determination is best measure of progress of patient.

B. SPECIFIC MEDICAL PROCEDURES:

(1) *Preplacement:* Individuals suffering from anemia or cardiovascular or pulmonary disabilities should not be employed for work with dinitrobenzene.

(2) *Periodic:* Medical inspection of personnel is desirable. Medical assistance should be within immediate call at all times. Examination of the urine may be helpful in the periodic inspection.

V. References

1. American Conference of Governmental Industrial Hygienists: *AMA Arch. Ind. Health 18:* 178 (1958).
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Heptane

(n-Heptane)

I. Hygienic Standards

A. RECOMMENDED MAXIMUM ATMOSPHERIC CONENTRATION (8 hours): 500 parts of vapor per million parts of air, by volume (ppm).[1]

(1) *Basis for recommendation:* Sensory response and comfort from limited human sensory data and by analogy with the better studied gasoline. The 500 ppm threshold limit is believed to be low enough to prevent narcosis and mucous membrane irritation.

B. SEVERITY OF HAZARDS:

(1) *Health:* Low, for both acute and chronic exposures. The paraffin hydrocarbons are anesthetic agents, and irritate mucous membrane, but do not cause systemic toxicity. Exposure to high concentrations produces dizziness, intoxication, and slight nausea, with loss of appetite. Narcosis is the most important effect of exposure.

(2) *Fire:* Severe. Explosive limits are 1.0 to 6.0% by volume. Flash point is −3.9°C (25°F) (closed cup).

C. SHORT EXPOSURE TOLERANCE: Men developed slight dizziness within six minutes while inhaling 1,000 ppm in air.[2] Exposure to 5,000 ppm for 15 minutes resulted in a condition resembling intoxication from ethyl alcohol.

D. ATMOSPHERIC CONCENTRATIONS IMMEDIATELY HAZARDOUS TO LIFE: Unknown for man. The lethal concentration for mice has been reported as 65 mg/liter (15,900 ppm) for 30 minutes continuous exposure,[4] and 78 mg/liter (18,337 ppm) for two hours continuous exposure.[5]

II. Significant Properties

A clear, colorless, volatile liquid, highly flammable with a faint characteristic odor.

Chemical formula:	$CH_3(CH_2)_5CH_3$
Molecular weight:	100.2
Specific gravity:	0.6837 (20°/4°C)
Boiling point:	98.43° C
Relative vapor density:	3.46 (air = 1)
Solubility:	Soluble in ether and chloroform, insoluble in water.
At 25°C and 760 mm Hg,	
1 ppm of vapor:	0.00409 mg/liter
1 mg/liter of vapor:	244.5 ppm

III. Industrial Hygiene Practice

A. RECOGNITION: Used as a solvent and as a standard in testing knock of gasoline engines.

B. EVALUATION OF EXPOSURE:

(1) *Direct instrumentation:* Determination by the use of combustion-type meters, suitably calibrated.

(2) *Chemical method:*[3, 6] Adsorption on silica gel or activated carbon followed by desorption and analysis by gas chromatography.

C. RECOMMENDED CONTROL PROCEDURES: Maintain workroom atmospheres below 500 ppm. Good general ventilation and enclosure of processes will normally maintain workroom atmospheric concentrations below recommended level. With elevated temperatures, process ventilation may be required. Skin contact should be avoided due to drying action on the skin.

IV. Specific Procedures

A. FIRST AID: While exposure to vapors in sufficient quantity to produce asphyxia or central nervous system depression is not expected, should such occur, the usual procedures of removal from exposure, artificial respiration and use of oxygen would be indicated. Eyes, if splashed, should be immediately washed with copious quantities of water for at least 15 minutes, and then seen by a physician.

B. SPECIAL MEDICAL PROCEDURES: None.

V. References

1. American Conference of Governmental Industrial Hygienists: *AMA Arch. of Ind. Health 18:* 179 (1958).

2. PATTY, F. A., and W. P. YANT: *U. S. Bureau of Mines Repts. Investigations No. 2979.* (1929).
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Hexane

(n-Hexane)

I. Hygienic Standards

A. RECOMMENDED MAXIMUM ATMOSPHERIC CONCENTRATION (8 hours): 500 parts of vapor per million parts of air, by volume (ppm).[2]

(1) *Basis for recommendation:* Sensory response and comfort from limited human sensory data, and by analogy with the better studied gasoline. The 500 ppm threshold limit is believed to be low enough to prevent narcosis and mucous membrane irritation. (NOTE: Some commercial or technical grade hexanes may contain benzene in amounts which might cause excessive atmospheric benzene (benzol) concentrations, over 25 ppm. In such cases, the permissible limit for benzene would take precedence.)

B. SEVERITY OF HAZARDS:

(1) *Health:*[7] Hexane is marketed in varying grades of purity, ranging from the very pure (essentially 100% n-hexane) to the technical or commercial (45–86% n-hexane, with isohexanes and cyclopentanes as the principal remaining constituents). The technical or commercial grades may also contain benzene (benzol) from less than 1% to as much as 6%. This must be considered in evaluating the hexane health hazard:

(a) n-Hexane and commercial or technical grades essentially free of benzene: Low, for both acute and chronic exposures. The paraffin hydrocarbons are anesthetic agents and irritate mucous membrane, but do not cause systemic toxicity. Unacclimatized subjects found no irritation at 500 ppm,[3] but nausea, headache, eye and throat irritation were reported at 1400 to 1500 ppm.[2] Narcosis is the most important effect of exposure.

(b) Technical or commercial grades containing appreciable benzene: Low, for acute exposure; low to moderate, for chronic exposure, depending on the amount of benzene present. (See Hygienic Guide for Benzene.)

(2) *Fire:* Severe. Explosive limits are 1.3 to 6.9% by volume. Flash point is −25.7°C (−14.4°F) open cup and −21.6°C (−7°F) closed cup.

C. SHORT EXPOSURE TOLERANCE: Narcosis of mice was caused in less than one hour by concentrations of about 3% by volume (30,000 ppm) and convulsions and death occurred in a similar time in concentrations of 3.5 to 4%.[4] With men, 0.2% (2000 ppm) produced no symptoms in ten minutes, while 0.5% caused distinct dizziness and giddiness.[5]

D. ATMOSPHERIC CONCENTRATION IMMEDIATELY HAZARDOUS TO LIFE: Unknown for man. The lethal concentration for mice has been reported as 154 mg/liter (43,700 ppm),[5] and 120 to 150 mg/liter (34,000 to 42,600 ppm)[6] for two hours continuous exposure.

II. Significant Properties

A clear, colorless, volatile liquid, highly flammable, with a faint characteristic odor.

Chemical formula:	$CH_3(CH_2)_4CH_3$
Molecular weight:	86.17
Specific gravity:	0.6603 (20°/4°C)
Boiling point:	68.74°C (66° to 71°C in commercial grades)
Relative vapor density:	2.97 (air = 1)

Solubility:	Soluble in ether and chloroform; insoluble in water.
At 25°C and 760 mm Hg,	
1 ppm of vapor:	0.00352 mg/liter
1 mg/liter of vapor:	284 ppm

III. Industrial Hygiene Practice

A. RECOGNITION: Used as a solvent (especially in the extraction of edible fats and oils), a laboratory reagent, and as the liquid in low temperature thermometers.

B. EVALUATION OF EXPOSURE:

(1) *Direct instrumentation:* Determination by the use of combustion-type meters, suitably calibrated.

(2) *Chemical method:*[6, 10] Adsorption on silica gel or activated carbon followed by desorption and analysis by gas chromatography. (NOTE: For evaluation of benzene exposure, if present, see Hygienic Guide for Benzene (Benzol).)

C. RECOMMENDED CONTROL MEASURES: Maintain workroom atmospheres below 500 ppm. Good general ventilation and enclosure of processes will normally maintain workroom atmospheric concentrations below recommended level. With elevated temperatures, process ventilation may be required. Skin contact should be avoided due to drying action on the skin. If benzene is present and exceeds 25 parts per million parts of air, control by means of process enclosure and/or ventilation.

IV. Specific Procedures

A. FIRST AID: While exposure to vapors in sufficient quantity to produce asphyxia or central nervous system depression is not expected, should such occur, the usual procedures of removal from exposure, artificial respiration and use of oxygen would be indicated. Eyes, if splashed, should be immediately washed with copious quantities of water for at least 15 minutes and then seen by a physician.

B. SPECIAL MEDICAL PROCEDURES: None, unless benzene atmospheric concentration exceeds 35 ppm, then see Hygienic Guide for Benzene.

V. References

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Because of space limitations, it is impossible to list all methods of exposure evaluation. The selections have been made on the basis of current usage, reliability, and applicability to the usual industrial type of exposure. Any specific evaluation and/or control problem will involve professional judgment. This can best be done by professional industrial hydigene personnel.

Respiratory protective devices are commercially available. Their use, however, should be confined to emergency or intermittent exposures and not relied upon as primary means of hazard control.

A relative scale is used for rating the severity of hazards: nil, low, moderate, high, and extra hazardous.

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